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

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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.

Keywords

Biomaterials; oxides; plasma deposition; electrochemical techniques; electrochemical properties

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

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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 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 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 (0.12M), calcium acetate Ca(CH₃COO)₂ (0.075M), and Ca(H₂PO₄)₂.H₂O (0.025M) 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 minutes were selected to accomplish the PEO process.

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 behaviour 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 minutes 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 -750mV 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

Figure 1 and Figure 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 to 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 (Figure 3 and Figure 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.

3.2 Electrochemical testing

Open circuit potential (OCP)—Open circuit potential variations with time are related to the nature of reactions at the surface of the electrode when in contact with a specific medium (passivation, dissolution or immunity) and therefore can be used as a criterion for corrosion behavior. Figure 5 shows the typical OCP variations with respect to time for the untreated γ TiAl and Ti6Al4V alloy and the corresponding comparison with some of the PEO treated samples in SBF. The initial OCP for the bare γ TiAl and Ti6Al4V alloys is -129 mV (vs. V_{SCE}) and -264 mV (vs. V_{SCE}) respectively, which indicates a higher resistance to corrosion of γ TiAl over Ti6Al4V when in contact with SBF. However, the profiles obtained for both alloys exhibit a consistent increase towards more positive potential until a quasi-stationary value is reached. Results obtained in similar studies for titanium alloys in contact with Hank's solution or SBF [26, 41, 42] indicate that this change is related to the formation of an oxide film that passivates the metallic surface. On the other hand, OCP profiles for PEO treated γ TiAl and Ti6Al4V samples exhibited very stable potentials during the test. The trend towards more noble potentials is not as considerable as for the untreated samples. Although the coatings obtained in both treated alloys are highly porous, and some localized dissolution phenomena can be expected, none of the samples under study exhibited potential drops associated with surface dissolution during the testing period.

Cyclic polarization (CP)—The increased ion release rate due to different forms of localized corrosion, may lead to a series of undesirable biological responses and eventually, implant loosening [8]. Susceptibility to these forms of corrosion is evaluated by DC techniques such as cyclic polarization. The parameters obtained from the current-voltage curve can be associated with the localized corrosion mechanism. The breakdown voltage (E_b) corresponds to the potential where the current density rapidly increases after the passivation zone, leading to pit nucleation and propagation through the substrate surface

[33]. The pits continue to grow until the repassivation potential (E_{prot}) is reached where the loop is closed. At this potential, the passive layer is rebuilt over the pits thus stopping localized metal dissolution [26, 33]. In that order breakdown potential is a sign of localized corrosion, but the measure of pitting susceptibility is the difference between the breakdown and the repassivation potential (the hysteresis loop area). Figure 6 shows the polarization curves obtained for untreated γTiAl and Ti6Al4V in SBF. Significant differences were observed between the curves obtained for each alloy. For the γTiAl alloy, the breakdown potential is found at 678mV (vs. V_{SCE}) while no evidence of breakdown and pit formation (even at high potentials) was evident in the polarization curves obtained for Ti6Al4V alloy, thus implying the higher resistance of the latter alloy to this localized corrosion phenomena. Similar results have been previously reported by Delgado et al [43, 44]. Additionally, the hysteresis loop area observed for the γTiAl alloy is a direct measurement of the significant pitting susceptibility of the alloy under the conditions evaluated. It has been suggested that the breakdown of the passive film is due to the higher Al content in the alloy [45]. To compare the susceptibility to pitting corrosion of the PEO treated specimens in relation to the untreated alloy, cyclic polarization studies were also performed on these samples. Figure 7 shows the cyclic polarization curves obtained for PEO treated γTiAl samples. As noted in the figure, the extent of the hysteresis loop is highly reduced and therefore, the corrosion mechanism operating on the substrate surface is less active when the coating is applied. Similar results have been reported for PEO Ti6Al4V alloy [29], thus underscoring the highly protective nature of the coatings obtained through this method. For all the PEO conditions applied, the negative hysteresis loop indicates that the passive film in the modified surfaces in the γTiAl alloy is resistant to localized pitting corrosion under the experimental conditions applied. No sign of film breakdown and consequently metal dissolution was evident. However, corrosion potential (E_{corr}) and corrosion current densities (i_{corr}) changed as PEO process parameters changed.

The corrosion potential (E_{corr}) and the corrosion current density (i_{corr}) were determined from the cyclic polarization tests and these are tabulated (see Table 3). The determination of corrosion parameters is carried out through the use of Gamry EChem Analyst Software® which automatically applies curve fitting to the data based on best fit. It must be clearly noted that since the corrosion phenomena in the only case of the untreated γTiAl alloys does not involve uniform corrosion and pitting in the observed corrosion mode, a rigorous analysis to take into account localized corrosion in the determination of the corrosion parameters was not attempted. As mentioned earlier, the data presented is the average based on three samples tested for each experimental condition. The values obtained are quite consistent and the variations in the values are small keeping in mind the random nature of the PEO process itself, porosity of the oxide coatings and local inhomogeneity of the samples.

The values of E_{corr} and i_{corr} obtained for the untreated alloys indicated lower corrosion rate and higher E_{corr} values for the γTiAl specimen (6.96 $\mu\text{A}/\text{cm}^2$, -152mV (vs. V_{SCE})) when compared with Ti6Al4V (25.6 $\mu\text{A}/\text{cm}^2$, -184.4V (vs. V_{SCE})). Although these results are in agreement with the behavior of the samples during the OCP measurements, the values are different from those obtained in the OCP tests, probably due to the change in the nature of

the passive film (film thickness increases) during the cyclic polarization scan, a phenomenon reported elsewhere [34].

A significant effect in enhancing the corrosion resistance of the alloy was noticeable as a result of the PEO process on γ TiAl. In general, the corrosion current density values obtained for PEO treated γ TiAl samples were lower ($0.5\text{--}21\text{ }\mu\text{A}/\text{cm}^2$) than the values for Ti6Al4V ($25\text{--}120\text{ }\mu\text{A}/\text{cm}^2$). Although there was a significant increase in E_{corr} and concomitant decrease in i_{corr} values for specific PEO parameters used to modify the surface of the titanium alloys under study, a few PEO treated samples bucked the trend and showed relatively increased degradation rates through the passive film when the material was coated and enriched with calcium and phosphorous ions. This result is in agreement with other studies on the corrosion resistance of Ca/P coatings on titanium alloys by Souto et al [46]. It is reported that hydroxyapatite coated titanium alloys showed increased metal dissolution in the system through the passive film. Related studies by Sousa et al [47] indicate that the higher current density values are the result of metal substrate dissolution and subsequent precipitation as hydrated salts on the film surface, which has been claimed to result in enhanced corrosion resistance of the underlying metal. However, conventional electrochemical techniques do not allow for distinguishing between these two cases, to establish whether metal ion release is enhanced or hindered for hydroxyapatite coated titanium substrates.

Corrosion resistance (affected by film features) is expected to increase for longer deposition time or increased current density during the PEO process. In our study, such a consistent trend in corrosion behavior was not detected. This is attributed to the dependence of the film features on subtle changes in PEO process parameters and the uneven surfaces attained in some of the conditions due to successive breakdown of the film. The cyclic nature of the PEO process where the anodic oxide first created is broken down and later reformed albeit at a fixed current density during the process time results in a multilayered coating growth which in turn results in an inconsistency in the measured corrosion parameters. However, the corrosion properties of samples treated under the same PEO process conditions and times are quite similar highlighted by the small standard deviation in the data.

Electrochemical impedance spectroscopy (EIS)—Electrochemical impedance spectroscopy was employed to investigate the effect of the PEO treatment on the corrosion behavior of each alloy studied. The results are analyzed to understand the interactions taking place between the modified alloy and the Ca/P rich environment in which they are in contact in SBF. Bode plots for the PEO treated and bare γ TiAl alloy are presented in Figure 8 and Figure 9. Analysis of these plots is made taking into account three frequency regions referred to as the high ($> 10000\text{ Hz}$), intermediate (10000 Hz to 10 Hz) and low frequency ($< 10\text{ Hz}$) ranges that are obtained from impedance spectra. The comparison of the Bode phase plots of the untreated and coated γ TiAl can be appreciated in Figure 8. For the bare γ TiAl alloy the phase angle drops to zero at high frequencies indicating that the impedance is dominated by the solution resistance in this frequency range [48]. In the intermediate region, the phase angle remains close to -90° , indicative of the thin passive oxide film spontaneously formed on the surface. These particular features are closely related to the impedance modulus plot (Fig. 9), since the slope of the curve is -1 over the same

intermediate frequency region, which is also a characteristic response of a capacitive behavior of the surface film [41, 45].

The effects of the surface treatment on the electrochemical behavior of this alloy are noticeable in both Figure 8 and Figure 9. For the PEO treated samples, the phase angle responses as a whole shift toward higher frequencies, which indicates a decrease in the capacitance of the film formed as a result of the plasma electrolytic process. Other studies have related this phase angle shift to the presence of a thicker oxide film when compared with the naturally formed oxide on the γ TiAl surface [49]. A detailed study carried out by Hodgson et al [50] with reference to the interaction of titanium alloys with the calcium and phosphorous ions in SBF, concluded that the phase angle shift is a clear indication of the interactions of these ions in the electrolytic medium (SBF) with the metal surface. It must be emphasized that the shift of the phase angle in the aforementioned study is not as significant as noted in our study, implying that this phenomenon in our case is mostly a result of a more protective PEO layer. It also appears that this protection dominates over a greater frequency range compared to the untreated alloy highlighting the effectiveness of the PEO film against corrosion in SBF.

The impedance modulus $|Z|$ quantifies the corrosion resistance of the metal/coating structure. Figure 9 shows the comparison for the untreated γ TiAl and the PEO treated samples, showing a clear increase in this value at low frequencies thus underlining the beneficial effect of the coatings in terms of enhancing the corrosion properties of the alloy and the protective action of the coating against chemical degradation. Additionally, the effect of different PEO treatment conditions on impedance values is noticeable, with relatively higher impedance compared to the value observed for the untreated specimen.

In the case of modified Ti6Al4V alloys, a similar response to PEO treatments was observed. The increase in corrosion resistance denoted by higher values of resistance and lower capacitance values, in addition to the phase angle shift as an indication of the chemical interaction with the ions in SBF was highly noticeable. However, significant differences with regard to the phenomena taking place at the metal substrate/electrolyte interface for the untreated γ TiAl and Ti6Al4V were evident from the Nyquist plot comparison (Figure 10 and Figure 11). For Ti6Al4V alloy, the Nyquist plot in Figure 10 indicates one semicircle associated with the double layer capacitance of the metal substrate, and a single time constant is derived from the graphical interpretation, in agreement with results reported earlier [51, 52]. On the other hand, the impedance spectra for the γ TiAl alloy (Figure 11) shows 2 semicircles overlapped and depressed implying two time constants corresponding to two different electrochemical processes. Besides the values for impedance for the PEO treated γ TiAl alloys were much higher compared to PEO treated Ti6Al4V.

4. Discussion

The PEO process results in the formation of a protective oxide layer through anodization in the initial stages. A continued application of the high voltage results in the breakdown of this compact oxide layer into a porous structure of the oxide coating due to the resultant microarcing. This is then followed by subsequent healing of the oxide. Prolonged treatment

will result in this cyclic process of initial compact oxide formation, followed by the development of a porous oxide structure and subsequent healing and consolidation of this porous layer. It is imperative that this phenomenon should be taken into account while analyzing the resultant impedance spectra from EIS testing. The thickness of the resulting compact oxide layer, and the size of the overlying porous oxide layer along with the density and size of pores vary depending on the applied current density and corresponding voltage. In the case of Ti6Al4V, rather large pores are formed while for γ TiAl submicron size pores are observed. Pores within this submicron diameter range have been shown to be far more effective in inducing apatite formation [15, 16], indicating the benefit of PEO coatings on γ TiAl. Several studies regarding the effect of pore size on titanium treated surfaces have demonstrated that smaller pores on titanium surfaces can enhance the proliferation of human bone cells in contrast to larger pores [40, 53]. Previous studies have indicated the effect of variables such as electrolyte [54], or applied voltage used in plasma electrolysis on morphology, roughness of the coatings, or the composition of the oxides formed on titanium and its alloy [23, 25]. Immersion tests carried out with titanium surfaces in solutions that include calcium and phosphorous ions have shown the role of these bioactive surfaces in the precipitation of calcium phosphate phases [55]. Moreover, augmented biocompatibility of Ca-P coated metallic implants have been reported elsewhere thus highlighting the advantage of applying PEO on titanium alloys under the conditions described [22, 24, 27, 54].

PEO coatings certainly modify the corrosion protection characteristics of the native oxides on the Ti alloy surfaces, since the open circuit potentials obtained are higher when compared with untreated samples. Similar results have been also reported for alloys subjected to anodic oxidation and ceramic coatings [56, 57] suggesting that such coatings indeed enhance corrosion resistance of titanium biomaterials. From the present study, results demonstrate that PEO treated samples for both alloys under study were electrochemically less active in comparison to untreated metals and alloys. This behavior suggests that the oxide film resulting from the PEO process increases the resistance of these Ti alloys to chemical dissolution in SBF.

γ TiAl appears to be more corrosion resistant compared to Ti6Al4V even without the PEO coating in SBF. The lower corrosion current density value obtained for the γ TiAl alloy might be due to the effect of Nb in the passive film formed. The effects of Nb as an alloying element in stabilizing the surface films of the Ti based alloys have been reported by Souto et al [46] and Khan et al [51]. The Nb cations improve the passivation properties of the film by decreasing the concentration of anion vacancies present on titanium oxide films. These anion vacancies are generated by the presence of lower titanium oxidation states [45, 51, 58]. Other hypotheses to the superior corrosion properties in alloys with Nb as an alloying element are related to the fact that its corrosion products are less soluble compared to those of vanadium [51]. Better corrosion performance of different titanium alloys containing Nb with respect to Ti6Al4V alloy in different media solution have been reported [45, 58]. Comparatively, the impedance values (and consequently corrosion resistance) for the modified γ TiAl samples were higher than values observed for PEO treated Ti6Al4V samples. It has been reported that the vanadium oxide formed on the surface of Ti6Al4V alloy dissolves and leaves defects resulting in diffusion of vacancies in the surface film and also that this process is further enhanced by the presence of Cl^- ions [49]. As such, this

phenomenon can account for the significant differences in the impedance values for the alloys under study, in particular due to the composition of the oxides formed by PEO process.

As established earlier, the properties of the PEO coating are strongly dependent on the process parameters used, and are also specific for each titanium alloy. The corrosion behavior of the materials is related to the properties of their passive layer [26, 33, 45, 58] and therefore it can be expected that corrosion properties change based upon the PEO process conditions applied (Table 2). Thus, some slight differences are obtained in the present study for the potentials when comparing the OCP values to those from the cyclic polarization tests. Nevertheless, the PEO process clearly increases the corrosion resistance of the γ TiAl alloy indicating the protective nature of the oxide formed.

The enhancement of corrosion characteristics of different titanium alloys under different surface modifications have been reported elsewhere [44, 49, 52, 59]. EIS results obtained by Shukla et al [49] on commercially pure titanium, Ti6Al4V and Ti6Al7Nb under alkaline treatment suggest the advantages of these treatments in order to increase surface reactivity towards apatite formation. Further, laser pulsed treatments carried out by Zaveri et al [59] and thermal oxidation of titanium alloys performed by Delgado et al [44] have shown the protective nature of the films and their stability against corrosion degradation by exhibiting increased polarization resistance values. The interactions of titanium alloys in contact with simulated biological fluids and the charge distribution phenomena due to the double layer structure have been widely reported [41, 49]. The double layer is present due to hydroxyl ions (OH^-) at the metal surface, and charge transfer can occur within the layer depending on whether the metal oxide is stable or whether it is passivating [49]. Taking into account the results from OCP and CP tests, it is clear that the metal surfaces for both Ti alloys in this study are passivating. However, the extent of this phenomena seems to be broader for the γ TiAl and the PEO treated samples, which can account for the second time constant (second semicircle in Nyquist plot) in the present study. Moreover, the effect of the PEO process is appreciated in the Nyquist plot for both γ TiAl and Ti6Al4V alloys (Figure 10 and Figure 11). Analogous to the IZI values and its inference of enhanced corrosion resistance, the amplitudes of these semicircles is directly related with impedance values. Differences in the semicircle amplitude are observed as PEO process parameters change, which can be related to the dielectric properties of the oxide film formed. Similar results were observed by Delgado et al [48] when modifying the surface of γ TiAl and Ti6Al4V by means of thermal oxidation. It was found that the properties of the oxide layer changed depending on the oxidation temperature, and thus the amplitude of the corresponding arc in the Nyquist plot.

Due to the aforementioned differences in the impedance spectra for the two Ti alloys in this study, two electrically equivalent circuits are proposed to fit the experimental data. The electrochemical interface of Ti6Al4V alloy immersed in SBF solution can be described by the electrical equivalent circuit model in Figure 12. This model is a simple RQ circuit (Randles equivalent circuit), where a constant phase element (C_{dl}) with the charge transfer resistance (R_{ct}) accounts for the passive film properties, with R_s being the solution resistance. EIS data for the bare γ TiAl alloy and all the PEO treated samples showed a second time constant, and therefore, a different equivalent circuit is used to fit the data

(Figure 13). The parallel circuit elements proposed to model this behavior can be explained physically as the concurrent interaction of SBF with a bi-layered structural oxide layer. R_{porous} and C_{porous} account for the porous oxide layer while R_{inner} and C_{inner} account for the inner compact oxide layer in contact with the electrolyte. Again, in this case also constant phase elements rather than ideal capacitors have been justified based on the depressed arcs obtained in the Nyquist plots. The presence of this double layer structure has been reported previously by different authors [46, 47, 51, 58, 59]. EIS spectra of untreated titanium alloys (Ti6Al7Nb, Ti13Nb13Zr and Ti35Nb among others) immersed in Hank's and SBF solutions, present similar features to those observed in Bode and Nyquist plots for PEO treated alloys in the current study. Previous studies [47, 52, 59] again attribute this behavior to a double layer structure consisting of a porous outer layer and a barrier inner layer where interaction of both compact and porous layer within the SBF electrolyte is occurring simultaneously. The appearance of a second time constant as a consequence of surface treatments to enhance corrosion resistance of titanium alloys has been reported [49, 59]. In addition, EIS data from Ti6Al4V alloy modified by passivation in nitric acid followed by plasma sprayed hydroxyapatite obtained by Souto et al [46], were fitted using an equivalent circuit with two time constants, one for a compact passive film and another for the porous hydroxyapatite layer.

A constant phase element, rather than an ideal capacitor, is used in the models due to the depressed arcs obtained in the Nyquist plot, which is possibly the result of the interaction or overlapping of more than one charge transfer phenomenon. The use of CPE to represent the interactions of Ti6Al4V with different fluids that simulate the body environment has been reported previously [41, 58, 59]. The impedance of this element is defined by $Z_{\text{CPE}} = 1/[Q(j\omega)^n]$ where the exponent n is related to the non-equilibrium current distribution due to the surface roughness and/or surface defects, $j\omega$ is the complex variable for sinusoidal perturbations with $\omega = 2\pi f$, Q represents the true capacitance of the oxide barrier layer and therefore the CPE represents deviation from ideal capacitor behavior [45, 46, 52]. Table 4 summarizes the values calculated for the equivalent circuit elements that describe the corrosion phenomena in PEO coated γ TiAl and Ti6Al4V. A goodness of fit more than 99% confidence was obtained when the data from EIS testing was fitted with the equivalent circuit elements using Gamry EChem Analyst Software®. n values (not tabulated) obtained for PEO coatings on Ti6Al4V alloy were lower (0.6–0.9) than those obtained for γ TiAl (~0.9–0.96). It has been reported that low n values (0.5–0.7) can be attributed to the roughness and irregularity of the coatings [46]. Shukla et al [49] suggest that n values of about 0.9 were indicative of near capacitive behavior of the films due to their regular and homogeneous nature. The morphological characterization discussed in the previous sections showed that PEO coatings on γ TiAl exhibits a relatively more compact layer structure, while in the case of Ti6Al4V alloy, highly porous and non-uniform layers are obtained, and consequently, lower n values are obtained.

In the case of Ti6Al4V, corrosion resistance properties change drastically with PEO process conditions, which is in agreement with the analysis made for the results of the cyclic polarization tests. This clearly suggests that the coating formed acts as a stable barrier to chemical degradation, thus improving corrosion resistance. Contrary to the results obtained for Ti6Al4V, impedance values obtained for γ TiAl were higher, even for the bare alloy,

while PEO treated alloys showed an increase in the impedance values, and consequently the corrosion resistance by a significant proportion. The changes in the resistance of the passive film on the material can be attributed to structural changes in the film or changes in the electrical conductivity of the film given the different conditions applied during the surface modification process. The results obtained by Hodgson et al [50] based on the electrochemical characterization of Ti6Al4V and Ti6Al7Nb passive films indicate that the significant differences in the semi-conductive properties of these films can be attributed to the variety of oxides from the alloying elements, namely $\text{Al}_2\text{O}_3\text{VO}_x\text{Nb}_2\text{O}_3\text{Nb}_2\text{O}_5$ in the semi-conductive TiO_2 . For example, Al_2O_3 is known to be an insulator whilst Nb_2O_3 and VO_x are semi-conductive in nature. The characterization of the PEO coating, its growth mechanism and the principal compositional and morphological features related to the process parameters used in each of the alloys under study were made by using different techniques [61]. Coating features were strongly dependent on the current density values and the resulting voltage for plasma electrolysis used and were specific to each alloy. Thus for some cases for PEO treatment when one expects a consolidated inner oxide layer vis-à-vis a porous outer layer, the latter may result to be relatively more compact resulting in a higher value of impedance and hence it may indeed be more appropriate to report optimum process parameters for the PEO treatment.

Nevertheless, electrochemical analysis showed the significant effect of these surface modifications from PEO treatment on the corrosion performance of both alloys. Generally, the PEO coatings enhanced the corrosion resistance of the Ti alloys, acting as a stable barrier against chemical degradation on exposure to SBF.

5. Conclusions

1. Open circuit potential curves obtained for PEO treated samples demonstrated that coated samples are electrochemically less active in comparison to untreated metals.
2. PEO coatings formed on γTiAl surface were able to reduce corrosion to a great extent due to the formation of a consolidated oxide layer for the PEO treated TiAl alloy. Ti6Al4V samples subjected to the same treatment exhibited a more porous layer, which could be attributed to higher corrosion rates observed for the latter.
3. Higher impedance values were obtained for the PEO treated γTiAl samples from EIS testing and therefore, increased corrosion resistance is attributed to γTiAl alloy in the PEO treated condition.

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Research Highlights

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

Figure 1.
SEM micrographs of γ TiAl surfaces after PEO process at different conditions.

Figure 2.
SEM micrographs of Ti6Al4V surfaces after PEO process at different conditions.

Figure 3.
Typical EDS spectrum of PEO treatment on γ TiAl: 152 mA/cm²+3min.

Figure 4.
Typical EDS spectrum of PEO treatment on Ti6Al4V 227 mA/cm²+4min.

Figure 5.
Open circuit potential (OCP) measurements for γ TiAl, Ti6Al4V and PEO treated samples in SBF media.

Figure 6.
Cyclic polarization curves for γ TiAl and Ti6Al4V samples in SBF media.

Figure 7.
Cyclic polarization curves for PEO treated γ TiAl samples in SBF media.

Figure 8.
Bode phase angle plots for PEO treated γ TiAl samples in SBF media.

Figure 9.

Bode impedance modulus for PEO treated γ TiAl samples in SBF media.

Figure 10.
Nyquist plots for PEO treated γTiAl samples in SBF media.

Figure 11.
Nyquist plots for PEO treated Ti6Al4V samples in SBF media.

Figure 12. Electrical equivalent circuit for bare Ti6Al4V alloy immersed in SBF. R_s represents solution resistance while CPE and R_{ct} correspond to the passive oxide layer.

Figure 13.

Electrical equivalent circuit for γ TiAl and PEO treated samples immersed in SBF. R_s represents solution resistance, CPE_{porous} and R_{porous} correspond to the porous oxide layer while CPE_{inner} and R_{inner} correspond to the inner oxide layer.

Table 1

Chemical composition of Calcium/Phosphorous rich electrolyte.

Reactant	Quantity
Na ₂ -EDTA	44.67g/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

Table 2

Current density and time values used in the PEO process to obtain the coatings on γ TiAl and Ti6Al4V alloys.

γ TiAl		Ti6Al4V	
Current Density [mA/cm ²]	Time [min]	Current Density [mA/cm ²]	Time [min]
133	3,4,5	152	2,3,4
152	3,4,5	189	2,3,4
171	3,4,5	227	2,3,4

Table 3

Corrosion parameters for PEO-treated γ TiAl and Ti6Al4V samples. Values for untreated samples are given for comparison.

Material	i_{corr} [$\mu\text{A}/\text{cm}^2$]	E_{corr} [mV]
γ TiAl	7.0 $\pm$ 0.42	-152 $\pm$ 14
133 mA/cm ² +3min	5.1 $\pm$ 0.635	-129 $\pm$ 6
133 mA/cm ² +4min	6.1 $\pm$ 0.59	-246 $\pm$ 5
133 mA/cm ² +5min	9.9 $\pm$ 1.08	-148 $\pm$ 7
152 mA/cm ² +3min	0.5 $\pm$ 0.092	-64.1 $\pm$ 2
152 mA/cm ² +4min	9.6 $\pm$ 0.83	-150 $\pm$ 4
152mA/cm ² +5min	20.6 $\pm$ 0.65	-239 $\pm$ 3
171 mA/cm ² +3min	8.7 $\pm$ 0.315	-175 $\pm$ 5
171 mA/cm ² +4min	7.1 $\pm$ 1.045	-200 $\pm$ 4
171 mA/cm ² +5min	0.9 $\pm$ 0.5295	-84.7 $\pm$ 4
Ti6Al4V	25.6 $\pm$ 2.1	-185 $\pm$ 1
152 mA/cm ² +2min	51.20 $\pm$ 6.83	-183 $\pm$ 4
152 mA/cm ² +3min	28.825 $\pm$ 0.31	-120 $\pm$ 19
152 mA/cm ² +4min	127.5 $\pm$ 18.5	-79 $\pm$ 2
189 mA/cm ² +2min	12.97 $\pm$ 7.23	-136 $\pm$ 11
189 mA/cm ² +3min	62.45 $\pm$ 3.45	-128 $\pm$ 9
189 mA/cm ² +4min	38.3 $\pm$ 1.5	-110 $\pm$ 5
227mA/cm ² +2min	5.460 $\pm$ 0.35	-175 $\pm$ 7
227 mA/cm ² +3min	12.45 $\pm$ 0.65	-70 $\pm$ 5
227 mA/cm ² +4min	8.66 $\pm$ 0.78	-234 $\pm$ 6

Table 4

EEC parameters (average values) for γ TiAl, Ti6Al4V and PEO treated specimens.

	R_s [$\Omega \cdot \text{cm}^2$]	R_{porous} [$\text{k}\Omega \cdot \text{cm}^2$]	C_{porous} [mF/cm^2]	R_{inner} [$\text{k}\Omega \cdot \text{cm}^2$]	C_{inner} [nF/cm^2]
γTiAl					
Untreated	19.63	2.47	1.87	7.70	9034
133 mA/cm ² +3min	16.00	3.86	13.46	12.31	22.50
133 mA/cm ² +4min	*	72.95	0.86	16.59	23.24
133 mA/cm ² +5min	*	38.74	11.90	15.74	20.24
152 mA/cm ² +3min	*	56.65	1.96	35.01	18.94
152 mA/cm ² +4min	*	42.58	27.88	12.31	21.75
152mA/cm ² +5min	5.78	4.27	3.35	15.75	23.91
171 mA/cm ² +3min	*	5.64	219.89	12.36	27.40
171 mA/cm ² +4min	*	44.82	2.56	93.32	10.67
171 mA/cm ² +5min	56.40	92.58	0.0003	104.85	16.93
Ti6Al4V					
Untreated	16.15	2.97	23.68	-	-
152 mA/cm ² +2min	4.06	1.84	3.88	5.84	44.70
152 mA/cm ² +3min	17.64	1.50	1.37	1.58	44.20
152 mA/cm ² +4min	14.71	1.24	0.45	0.86	37.17
189 mA/cm ² +2min	16.96	1.28	2.86	6.47	52.35
189 mA/cm ² +3min	15.15	1.64	1.11	12.69	81.83
189 mA/cm ² +4min	11.15	2.52	1.16	4.27	24.10
227 mA/cm ² +2min	17.14	1.49	2.57	11.83	53.35
227 mA/cm ² +3min	4.32	2.68	0.36	4.90	74.50
227 mA/cm ² +4min	9.47	2.81	0.93	10.08	130.57

* Could not be measured in the frequency range used