Electrochemical study of the corrosion of Ti-Pd and Ti-6Al-4V electrodes in sodium chloride solutions

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Summary

The electrochemical behavior of Ti-Pd and Ti-6Al-4V alloys in 0.9% NaCl solution were studied by single triangular potential sweep, potentiodynamic polarization curves, and electrochemical impedance spectroscopy techniques (EIS). The complicated corrosion mechanism can be interpreted as at least one electrodissolution process and the posterior formation of a corrosion films. The results from EIS indicate that, on each electrode, the corrosion layer is formed by different mechanisms.

Keywords: titanium, titanium alloys, corrosion resistance, electrochemical impedance

Introduction

Many materials have been used as surgical implants from 1860s. The use of non-noble metal, as titanium, in the plastic surgery of joints was not introduced until 1960s, after long research into the tolerability of the metal to organic tissues and cellular fluids in contact with it. The high strength-to-weigh ratio of titanium make it particularly suitable for the creation of substitute articulations such as hip prosthesis, and prosthodontic implants commonly referred to as "root form implants"[1-3]. Titanium-based alloys are attracting much attention for their favorable biocompatibility and corrosion resistance compared with conventional alloys as Co-Cr alloys and stainless steels. Corrosion resistance of titanium and its alloys in saline solutions, typical of physiological environments, is due to the formation of a protective oxide layers, mainly TiO_2, whose morphology depend on surface and thermochemical

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treatments of orthopedic material [4-6].

Most of the electrochemical research has been focused on crevice and pitting corrosion behavior of unalloyed titanium in sodium chloride solutions [7-11]. These investigations were related to applications involving the use of titanium for fabricating heat exchangers for service in seawater and in desalination plants. On the other hand, relatively little work has been done on the fundamental electrochemistry of titanium and its alloys *in vivo* and *in vitro* conditions. Correlation between results obtained under *in vivo* environments and those measured *in vitro* conditions has not been totally established [12]. However, discrepancies existent on the corrosion rate can be due to changes in Cl^- concentration, dissolved gaseous (O_2 and CO_2), and presence of microorganisms [12-17].

In view of the evidence of good clinical performance of titanium and titanium-based alloys it is essential to improve the understanding of the electrooxidation mechanism and of the effects alloying elements on corrosion process. Therefore, the present research aims to gain deeper insight into the mechanism of corrosion process of both biomaterials in 0.9% NaCl (physiologic serum), using potentiodynamic curves and electrochemical impedance spectroscopy.

Table 1. Chemical composition (weight %) of experimental biomaterials.

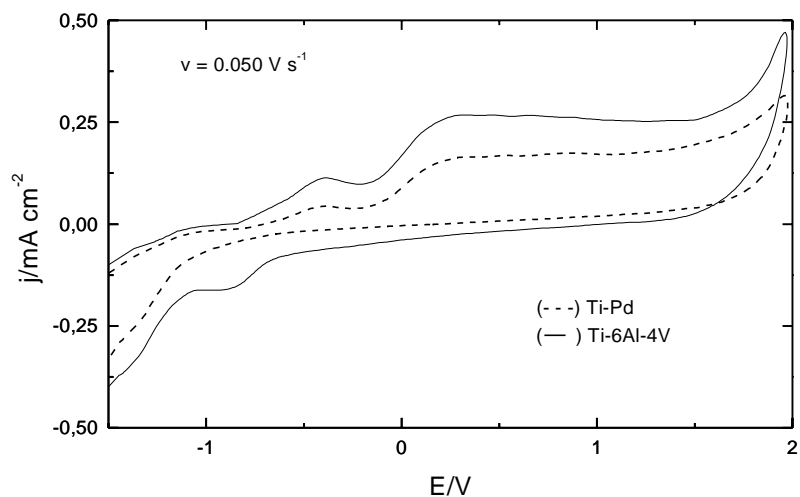| Elements	C	N	H	O	Fe	Al	Pd	V	Ti
Ti-Pd	0.12	0.004	0.015	0.20	0.28	-	0.18	-	balance
Ti-6Al-4V	0.02	0.006	0.004	0.19	0.17	6.10	-	4.0	balance

Figure 1. Comparative voltammograms of Ti-Pd (dashed curve) and Ti-6Al-4V (full curve) electrodes in 0.9% NaCl solution run, scan rate $v = 0.050$ V s^{-1}.
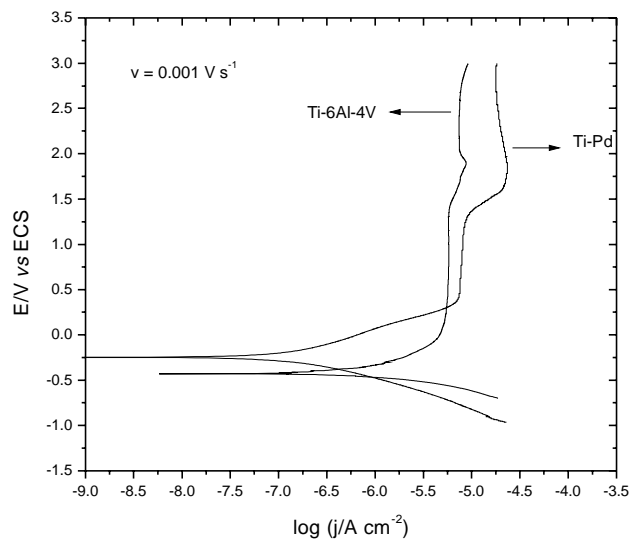

Figure 2. Potentiodynamic polarization curves for Ti-Pd and Ti-6Al-4V alloys, 0.9% NaCl, scan rate $v = 0.001$ V s^{-1}.

Table 2. Electrochemical parameters obtained from figure 2.

Biomaterials	E_{corr} (V)	j_{corr} (μA cm^{-2})	R_p (Ω cm^2)
Ti-Pd	-0.247 ± 0.02	0.6 ± 0.2	≈ 20000
Ti-6Al-4V	-0.425 ± 0.02	1.7 ± 0.2	≈ 18000

Materials and methods

In order to facilitate comparison of the Ti-Pd and Ti-6Al-4V currently in use for the manufacture of implants, a specimen of each type was selected for this investigation. Designation and chemical composition (weight %) of the metallic materials are shown in Table 1. These materials covers the chemical requirements of the standard specifications (ASTM) for surgical implant applications [18,19].

The experimental set-up for DC and AC measurements has been described in previous publications [20,21]. The electrochemical experiments were performed at 25 ^{0}C in conventional three-compartment double wall glass cell containing 0.9 wt.% NaCl solution (physiologic serum), which was prepared from analytical grade (p.a. Merck) reagents and deionized water. Ti-Pd and Ti-6Al-4V cylinders of across section 0.79 cm^2, were embedded in polyester resin Resapol T-208 holders and employed as working electrodes. These specimens were mechanically polished with 600 and 1200 grade emery papers, finished with 0.3 μm α-Al$_2$O$_3$, rinsed with deionized water and dried in air. The counter electrode was a graphite high purity cylinder, and the reference electrode was a saturated calomel electrode SCE (0.242 V *vs.* SHE). Electrochemical impedance spectroscopy (EIS) measurements were carried out using a Solartron 1255 FRA and 1287 EI integrated with a PC system. In this experiments, an additional activated platinum probe coupled to the reference electrode through a 10 μF capacitor is used to reduce phase shift errors at high frequencies. EIS data were collected at different polarization potential (-0.10 V ≤ E ≤ -0.50 V) in the frequency range between 100 kHz and 0.001 Hz with a signal amplitude of 0.01 V.

Results and Discussion

Potentiodynamic curves

The voltammograms of and Ti-6Al-4V in 0.9% NaCl at v = 0.050 V s^{-1} run between -1.5 V and 2.0V are show in figure 1. The potentiodynamic profiles are quali and quantitatively comparable. Additional current peaks due to presence of Al and V in Ti-6Al-4V was not observed. The similar voltammetric charge density suggests similar true surface area (roughness) offered by both electrodes.

The effect of Al and V on the electrochemical behavior of Ti in NaCl solution can be observed in the potentiodynamic polarization curves. Figure 2 shows these curves obtained at slow sweep rate (0.001 V s^{-1}) after the specimens were previously immersed into solution for 60 s. One of the first observations is that corrosion (E_{corr}) and pitting (E_{pit}) potentials appear at values more positive (≈0.25 V) for Ti-Pd. The electrochemical parameters obtained for the Tafel method are summarized in table 2. These data are results of three independent evaluations for each specimen. The calculated corrosion current densities (j_{corr}) indicates that the
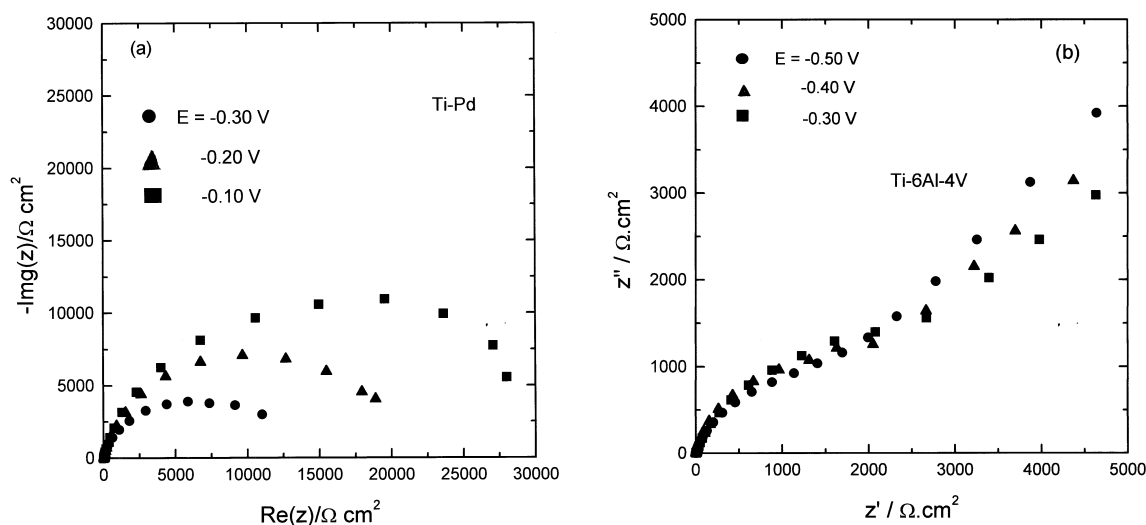

Figure 3. Nyquist diagrams of (a) Ti-Pd and (b) Ti-6Al-4V alloys at different applied potentials.

corrosion rate is greater for Ti-6Al-4V. Polarization resistance (R_p) values are lower than that reported for other authors [14]. However, R_p appears to be very affected by the immersion time and oxygen content in the electrolyte [14-17]. The chemical stability of Ti-Pd and Ti-6Al-4V in NaCl solutions is due to the formation of a protective oxides layer on the surface.

Electrochemical impedance spectroscopy measurements

The impedance responses of each investigated biomaterial were found to be different at the same applied potential. Nyquist diagrams recorded with Ti-Pd in 0.9% NaCl (Fig. 3) exhibit a capacitive semicircle at potential values close to the corrosion potential. As polarization potentials increases, the impedance $Z(j\omega)$ and the polarization resistance (R_p) values increases. This behavior can be associated with formation of a more compact and adherent oxides layer on the metal surface.

On the other hand, using Ti-6Al-4V electrode (Fig. 3), the complex plane plots display exhibits one slightly distorted capacitive semicircles and a second contribution at low frequencies (< 0.1 Hz). The shape of the last contribution can also be considered as a distorted semicircle with intersection in Re(Z) axis at very low frequencies (< 10^{-3} Hz), and can be related to slow process such as mass transport. The complicated alloys corrosion process can be interpreted as the sum of more than one electrodissolution process and the posterior formation of a corrosion films. If the concentration of dissolved metal cations close to the electrode

achieves a value at which oxides, hydroxides, or oxi-hydroxides precipitate, then corrosion process could become controlled by ionic transport (*ie*. Ti^{n+} n = 2, 3 or 4; or HO^-) through these porous precipitates.

In both types of electrodes, the electrolyte resistance $R_\Omega = \lim_{\omega \to \infty} |Z(j\omega)|$ is close to 7 Ω cm^2, and the estimated polarization resistance $R_p = \lim_{\omega \to 0} |Z(j\omega)|$ is in good agreement with that corresponding to previously calculated by Tafel method (see Table 2).

It has been demonstrated that in neutral solutions, under conditions where diffusion is restricted by surface films, allowance for the reversibility of the anodic reaction may significantly affect the calculated impedance spectra [22,23]. In general, the presence of surface films generates two time constants in an impedance spectrum. The first of these relates to the kinetics of the metal-metal ion reaction (the less noble metal) in parallel with a double layer capacitance and second arises from a finite length diffusional impedance. With the mass transport limited cathodic reduction of oxygen, this reaction path has a sufficiently high impedance to have almost no influence on the total impedance [23,24].

In the case of Ti-6Al-4V electrode, the high frequency response is due to the charge transfer resistance-double layer capacitance combination, and the lower frequency one is due to diffusional process through corrosion films. However, as the impedance response is dependent on the film thickness, probably, if thinnest films are formed on the Ti surface, the diffusional impedance occurs at
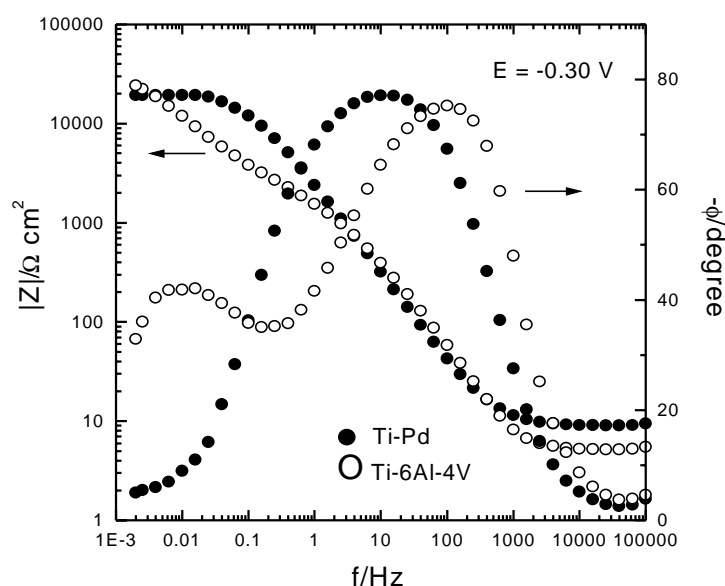

Figure 4. Comparison of the experimental Bode plots of Ti-Pd and Ti-6Al-4V alloys.

sufficiently high frequency that Nyquist plot appears to be a single semicircle.

One disadvantage of the display of experimental data in complex plane plots is the fact that the dependence of the impedance on the frequency of the applied signal is not directly shown. Therefore, bode plots for both biomaterials, at potential close to the corrosion potential, are shown in figure 4. The analysis of these plots confirm for Ti-6Al-4V the presence of two time constants in the 100 kHz - 1mHz frequency range.

Conclusions

The potentiodynamic response and EIS measurements indicate that the alloying elements have effect on the basic corrosion resistance of titanium in NaCl solution. An analysis of the experimental electrochemical data and calculated parameters for each system-specific indicate that the corrosion rate of Ti-Pd is mainly controlled by anodic electron transfer reaction involved en the metal electrodissolution process, whereas in Ti-6Al-4V, the kinetics of the electrodissolution reaction is controlled by diffusion of OH^- ions toward, or the oxidation products away from, the reaction sites through pores in the corrosion films.

Acknowledgements

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