

Corrosion Behavior Analysis of Plasma-assisted PVD Coated Ti-6Al-4V alloy in 2 M NaOH Solution

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The work aims the study of the corrosion behavior of nitride plasma-assisted PVD coated Ti-6Al-4V alloy in 2 M NaOH at 25 and 60°C, using open-circuit potential (OCP) versus time measurements, potentiodynamic polarization and electrochemical impedance spectroscopy (EIS). The uncoated Ti-6Al-4V alloy showed a passive behavior. The TiN and TiAlN/TiAlCrN coated Ti-6Al-4V alloy also presented a passive behavior and the corrosion potential remained at the same range when compared with the potential of the uncoated alloy. The TiN hard coating showed a superior corrosion resistance, which was evidenced by lower corrosion current densities and higher impedance values. The increase in temperature decreased the corrosion resistance of both uncoated and coated alloy in NaOH.

Keywords: Titanium, Polarization, EIS

1. Introduction

Various industries (like aerospace, biomedical, military, automotive and chemical) use titanium and its alloys. Due to their properties, they work in extreme conditions such as high temperature, corrosive environments and high strength^{1,2}.

About 80% of the global titanium amount produces aerospace parts such as gas turbines, wings and other load-bearing components. The other part acts in corrosive environments such as body fluid (pins, stents and artificial heart valves production), salty water (heat exchangers) and chemical media (compressor engine parts); and high temperatures^{1,3,4}.

Titanium alloys manufacture biomedical materials because of their low modulus, biocompatibility and superior corrosion resistance when compared to cobalt alloys and stainless steel. To provide better osseointegration, these pieces are usually treated with a bioinert material – hydroxyapatite¹.

Coating deposition on titanium alloys attracts attention by acting as barriers to the metallic diffusion. The corrosion products release metallic ions in the biological environment and may cause toxicity, allergy and mutagenicity⁵. Most of the transition metals form binary or ternary nitrides with good mechanical, tribological, protective and biocompatibility properties. In recent years, nitrides as TiN, ZrN, TiAlN, NbN, TaN and VN are used as protective layers against wear and corrosion in order to increase the prostheses and implants lifetime⁵. Cubillos *et al.*⁶ reported ZrN coated steel corrosion in NaCl solution due to pitting. The authors inform current densities ranged between 10^{-10} and 10^{-8} A/cm².

Fenker and colleagues⁷ studied NbN coated steel corrosion behavior and concluded that this coating increased steel corrosion behavior, closing pores with corrosion products during potentiodynamic test. Ma *et al.*⁸ showed TaN coated Cr12MoV polarization curves and informed potential value higher (-370 mV_{SCE} against -412 mV_{SCE}) and passive current density value lower (5×10^{-3} A/cm² against 4.5×10^{-2} A/cm²) than substrate values.

This paper is part of a series of electrochemical analyses that studied the corrosion behavior of TiN and TiAlN/TiAlCrN coated Ti-6Al-4V alloy, deposited by plasma-assisted PVD, in different corrosive environments and at different temperatures. Initially, the corrosion behavior of uncoated and coated Ti-6Al-4V alloy was studied in 2M HCl and 3.5 %wt NaCl solutions at 25, 60 and 80 °C^{9,10}. These studies, which was reported in the literature^{9,10}, showed that in HCl solution Ti-6Al-4V alloy demonstrated an active behaviour with an active-passive transition and coated Ti-6Al-4V alloy presented a passive behaviour. In NaCl solution, Ti-6Al-4V uncoated and coated alloy showed a passive behavior under all conditions. In both corrosive solutions, coated Ti-6Al-4V alloy showed a superior corrosion resistance with lower corrosion current densities and higher impedance values compared to the uncoated sample. It was also reported that increasing temperature decreased the corrosion resistance of the uncoated and coated Ti-6Al-4V alloy.

The present work aimed to investigate the corrosion behavior of TiN and TiAlN/TiAlCrN coated and uncoated Ti-6Al-4V alloy in 2M NaOH at 25 and 60 °C for biomedical and chemical applications.

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2. Materials and methods

The microstructure of Ti-6Al-4V alloy (5.980 wt.% Al, 0.005 wt.% C, 0.200 wt.% Fe, 0.001 wt.% H, 0.005 wt.% N, 0.001 wt.% O, 4.070 wt.% V and 89.738 wt.% Ti) was studied.

TiN and TiAlN/TiAlCrN based coatings (coated condition) were deposited on a total of 12 (twelve) specimens. The coatings were deposited by cathodic arc plasma assisted physical vapour deposition (PVD). The chamber has six cathodes or targets, which act as a highly-emitting area and present negative voltage relative to the chamber wall. Targets release the cathode material in the nitrogen plasma cloud where the reaction took place generating nitrides that were deposited on the substrate surface. TiN based coating is a single layer, which reached 2.2 μm of thickness (Figure 1a). TiAlN/TiAlCrN based coating is a multilayer, with 11 interfaces (TiAlN layers – 540 nm, TiAlCrN layers – 217 nm of thickness) and 6 μm of thickness (Figure 1b).

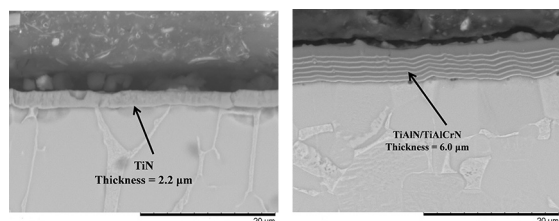


Figure 1. SEM images of PVD coated Ti-6Al-4V alloy microstructure (cross section): a) TiN and b) TiAlN/TiAlCrN.

Cylindrical specimens of 8 mm diameter and 17 mm in length were hot mounted in Teflon holders. The exposed uncoated surface area (0.5 cm²) was ground with SiC papers until 1200 grit, rinsed with distilled water and dried before transferring to the corrosive solution. The coated samples were not ground in order to maintain the coating integrity. The solution was 2 M NaOH, which was prepared using P.A reagents and distilled water. The temperatures were maintained at 25 and 60 °C. For the latter temperature, a thermostatic bath (FISATOM mod. 550) was used. The counter electrode was a platinum (Pt) foil. All potentials were referred to a saturated calomel electrode (SCE). The corrosion behavior of uncoated and coated Ti-6Al-4V alloys was studied using open-circuit potential vs. time (for three hours), electrochemical impedance spectroscopy (EIS) and potentiodynamic polarization. All measurements were performed using an Electrochemical Interface SOLARTRON mod. 1287 A and a Frequency Response Analyser SOLARTRON mod. 1260 A, controlled by the Ecorr/Zplot SOLARTRON mod. 125587S software. Data acquisition and analyses were performed using the same software.

3. Results and discussion

Figure 2 shows the open circuit potential versus time curve (OCP) obtained at room temperature (25 °C) and 60 °C

in 2 M NaOH solution of uncoated, TiN and TiAlN/TiAlCrN coated Ti-6Al-4V alloy. It demonstrates that the potential of uncoated Ti-6Al-4V alloy at 25 °C became more positive with time and tends to stabilize. This behavior suggests formation and growth of a passivating film. However, at 60 °C, the potential increases, reaches a maximum and moves towards negative potential, to also stabilize. This behavior suggests formation of a passivating film, but with less stability.

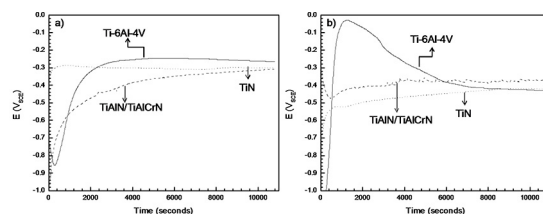


Figure 2. Open circuit potential vs. time for uncoated, TiN, and TiAlN/TiAlCrN coated Ti-6Al-4V alloy, in 2 M NaOH: a) at 25 °C, b) at 60 °C.

Figure 3 shows the anodic polarization curves of uncoated, TiN and TiAlN/TiAlCrN coated Ti-6Al-4V alloy in NaOH solution obtained at 25 and 60 °C. These curves represent the response in current form at a potential ranged from -0.5 to 2 V_{SCE} against E_{corr}. They tell us which is the material spontaneous behavior (if occurs spontaneous passivation or passivation under anodic polarization). They also inform us the passivating film stability and characteristic curve values such as i_{corr} and i_{pass} .

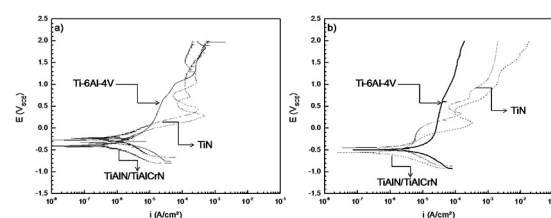


Figure 3. Potentiodynamic polarization curves for uncoated, TiN, and TiAlN/TiAlCrN coated Ti-6Al-4V alloy in 2 M NaOH: a) at 25 °C, b) at 60 °C.

Table 1 presents the main electrochemical parameters obtained from Figures 2 and Figure 3.

- Corrosion potential (E_{corr}) - indicate the material nobility;
- Null-current potential ($E_{i=0}$);
- Corrosion and passivation current densities (i_{corr} and i_{pass}) – these parameters are the material corrosion rate, so high current densities values means lower material resistance;
- Tafel slopes (β_a, β_c) – ensure linearity in i_{corr} measures.

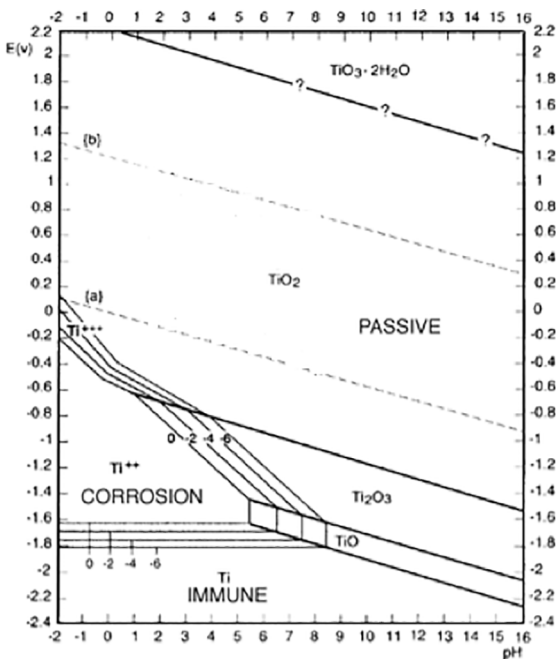
Figure 2 analysis together with titanium's Pourbaix diagram¹¹ (Figure 4) indicates that the corrosion potential ($-0.4 V_{\text{SHE}} < E_{\text{corr}} < -0.6 V_{\text{SHE}}$) in 2M NaOH solution, pH 10, is in the passivation region, which means passive behavior.

Table 1. Open circuit potential and polarization electrochemical parameters of uncoated, TiN and TiAlN/TiAlCrN coated Ti-6Al-4V alloy measured in at 25 and 60 °C.

Temperature (°C)	Sample	Parameters					
		E_{corr} (V_{SCE})	$E_{\text{f=0}}$ (V_{SCE})	i_{corr} (A/cm^2)	β_c (mV/decade)	β_a (mV/decade)	i_{pass} (A/cm^2)*
25	Ti-6Al-4V	-0.264	-0.323	6.2×10^{-7}	-93	102	2.1×10^{-5}
	TiN	-0.301	-0.233	2.1×10^{-7}	-192	192	-
	TiAlN/TiAlCrN	-0.309	-0.409	6.3×10^{-7}	-109	100	-
60	Ti-6Al-4V	-0.432	-0.499	2.2×10^{-6}	-80	112	3.6×10^{-5}
	TiN	-0.372	-0.449	1.3×10^{-6}	-76	114	-
	TiAlN/TiAlCrN	-0.422	-0.564	1.3×10^{-6}	-267	219	-

* measured in the middle of passive region.

Under anodic polarization, Figure 3a displays passive behavior of uncoated, TiN and TiAlN/TiAlCrN coated alloy at room temperature ($i < 9 \times 10^{-4} A/cm^2$). At 60 °C, Figure 3b shows active behavior at coated condition under anodic polarization.

**Figure 4.** Pourbaix diagram of titanium (V_{SHE} vs pH)¹¹.

For the uncoated alloy, the anodic current density increased from null-current potential at about $-0.323 V_{\text{SCE}}$ (Figure 3a) and $-0.499 V_{\text{SCE}}$ (Figure 3b) and sustained this behavior for higher potentials due to TiO_2 based film formation. TiO_2 delays titanium dissolution. The peak at $1.2 V_{\text{SCE}}$, showed in Figure 3a, was referred to transpassivation. The null-current potential should be more negative than the E_{corr} , because cathodic polarization tends to reduce surface oxides and make the surface less noble. Table 1 shows this trend. The anodic current density of coated alloys showed a behavior similar to one reported by Lunarska *et al.*¹² at both temperatures. Where, in a study about TiN coated steel

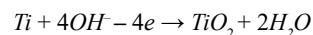
corrosion behavior in NaOH solution, at anodic potentials, the current increased until transpassivation happened. Increasing temperature reduced the corrosion resistance in all experimental conditions.

Even with the prior grinding process, titanium reacts with oxygen and form a TiO_2 based film. When the alloy immerses in a corrosive solution and remains at high potentials, the superficial film (formed by air) stabilizes on surface without undergoing dissolution. That means a more stable and protective film in corrosive solution. A material that behaves in this way is called spontaneously passive and this behavior has been observed by other authors who studied corrosion in NaOH solution.

E_{corr} values of this present work at uncoated condition were $-0.264 V_{\text{SCE}}$ at 25 °C and $-0.432 V_{\text{SCE}}$ at 60 °C. These results agree with Pjescic and collaborators¹³, who studied titanium's behavior in concentrated NaOH solutions, ranging from 1 to 5 M at 25 °C. Shahba *et al.*¹⁴ studied the electrochemical behavior of pure titanium and Ti-6Al-4V alloy in NaOH solutions at concentrations ranging from 0.5 to 0.001 M. They, however, found E_{corr} values ranged between -0.958 and $-0.735 V_{\text{SCE}}$ for pure titanium and between -0.858 to $-0.367 V_{\text{SCE}}$ for Ti-6Al-4V alloy.

According to Figure 2, TiN coated alloy sustained the potential, especially at 25 °C. At 60 °C, the potential begins high, falls and stabilizes at the same potential of uncoated Ti-6Al-4V. TiAlN/TiAlCrN coated alloy imitated TiN coated alloy behavior; except for OCP curve at 60 °C that displays potential drops during the test, typical of a defective layer. According to Rossi *et al.*¹⁵, the stability of nitride based coatings in corrosive media is due to their chemical inertness, which is normal for ceramic structures. Figure 5 shows the surface of the TiN and TiAlN/TiAlCrN coated alloy before potentiodynamic polarization.

TiO_2 is formed spontaneously on the surface of Ti-6Al-4V alloy when immersed in NaOH according to the following anodic reaction^{11,13}:



The cathodic reaction is related to the oxygen reduction¹⁴. According to Hefny *et al.* and Pjescic *et al.*^{13,16}, TiO_2 can be dissolved in alkaline solutions. However, the concentration

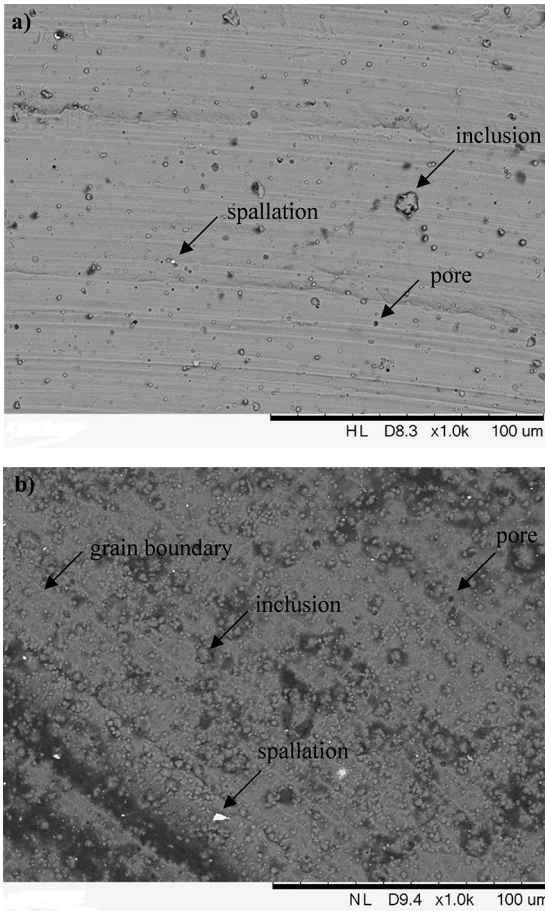
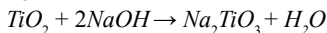


Figure 5. SEM images of PVD coated Ti-6Al-4V alloy surface before corrosion: a) TiN and b) TiAlN/TiAlCrN.

and temperature of such solutions are decisive for this reaction occurs. That is, TiO_2 turn into titanate, as shown in the following reaction:



Finally, at coated condition, Pohrellyuk¹⁷ described that when titanium nitrides behaves passively, it becomes an oxynitride, which is actively dissolved and oxidized to TiO_2 . This study, therefore, considers that under all experimental conditions it behaved passively due to stabilization (rather than dissolution) of TiO_2 at room temperature.

Electrochemical impedance spectroscopy measures ions flow resistance through the solution and working electrode. This measurement is done via a sine disturbance in potential and is read as lagged current in a characteristic phase angle. The Equations 1 and 2 correspond to the disturbance in potential and to the response in current^{18,19}.

$$E = E_0 \sin \omega t \quad (1)$$

$$I = I_0 \sin \omega t + \phi \quad (2)$$

where E is the oscillating voltage, E_0 is the amplitude of the oscillating voltage, I is the oscillating current, I_0 is

the amplitude of the oscillating current, ω is the angular frequency of disturbance and ϕ is the phase angle¹⁹.

Electrochemical impedance spectroscopy reflects the dielectric behavior, the oxi-reduction reactions and the mass transfer in the electrochemical interface (EI). Electrical and chemical properties of the corrosive solution and electrode material are related with the behavior of a specific EI. We adjust the impedance measurements using a equivalent electrical circuit that describes an EI. The EI's capacitive response usually comes from a non-ideal capacitor. Thus, a constant phase element (CPE) replaces pure capacitance according to Equation 3¹⁸⁻²⁰.

$$Z_{CPE} = [Y_0(j\omega)^n]^{-1} \quad (3)$$

where Y_0 [$F \cdot cm^{-2}$] and n ($n \leq 1$) are adjustable parameters. If the surface acts as an ideal capacitor, n is equal to one ($n = 1$), and Y_0 will be identical to capacitance C^{20} . We proposed two electrical circuit models for the conditions studied:

a) Uncoated Ti-6Al-4V:

Uncoated Ti-6Al-4V alloy behaved passively in NaOH solution indicating that the TiO_2 based layer is stable in the corrosive medium. This layer is made of a porous outer part and a compact inner one²¹. Thus, the equivalent circuit proposed in this present work for uncoated alloy has two time constants. The first time constant is related to outer porous layer and the second one is related to compact inner layer. The equivalent circuit and its components are: R_s as the corrosive solution resistance, R_g the outer porous layer resistance, C_g the outer porous layer pseudo-capacitance, R_p the compact inner layer resistance and C_p the compact inner layer pseudo-capacitance^{22,23}. The pseudo-capacitance represents superficial heterogeneities²³.

b) Coated TiN and TiAlN/TiAlCrN Ti-6Al-4V alloy:

Both TiN and TiAlN/TiAlCrN behaved passively. Nitride based coating are inert in any corrosive environment. The partial protective character of the nitride layers is due to the deposition method (PVD) that produces coatings with defects (pores, cracks, grain boundaries)^{24,25}. The coated alloy behaved according to the electrical equivalent circuit model with two time constants with the following elements: R_s corresponds to the corrosive solution resistance; R_c represents the defective coating (pores, cracks, grain boundaries) resistance to charge transfer; R_{ci} represents the charge transfer resistance at the coating/substrate interface. C_c and C_{di} represent the pseudo-capacitances at solution/coating and coating/substrate interfaces, respectively²⁴⁻²⁷.

Figure 6 shows the equivalent circuit and its components for uncoated and coated conditions.

Figure 7 shows Nyquist plots of uncoated Ti-6Al-4V alloy in 2 M NaOH solution at 25 to 60 °C.

Figure 8 shows Bode diagrams of uncoated Ti-6Al-4V alloy at 25 and 60 °C in 2 M NaOH.

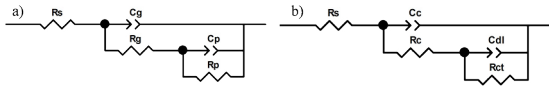


Figure 6. Electrical equivalent circuit proposed for: a) the uncoated Ti-6Al-4V alloy, b) the coated Ti-6Al-4V alloy, in NaOH solution.

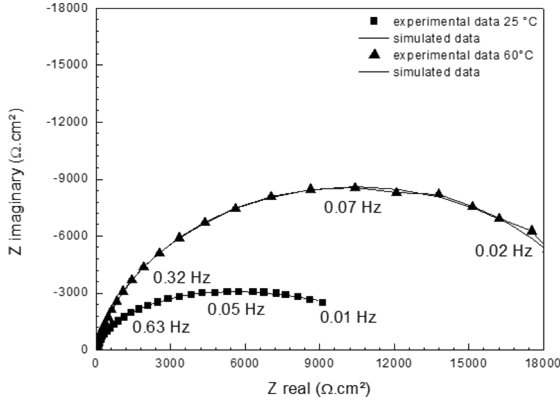


Figure 7. Nyquist diagram of uncoated Ti-6Al-4V alloy in 2 M NaOH at 25 and 60 °C.

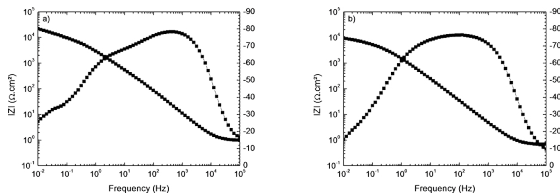


Figure 8. Bode diagrams of uncoated Ti-6Al-4V alloy in 2 M NaOH: a) at 25, b) at 60 °C.

Figures 9 and Figure 10 show the Nyquist plots of TiN and TiAlN/TiAlCrN coated Ti-6Al-4V alloy in 2 M NaOH, at 25 and 60 °C.

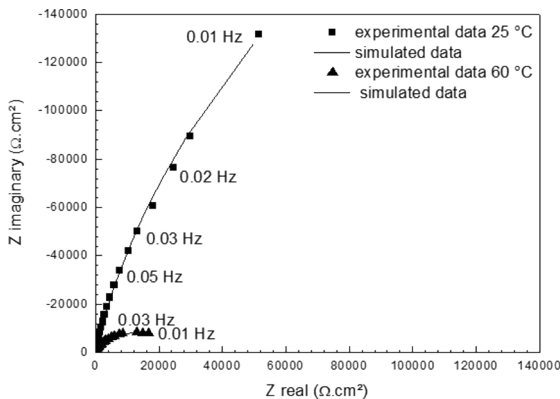


Figure 9. Nyquist diagram of TiN coated Ti-6Al-4V alloy in 2 M NaOH at 25 and 60 °C.

Figures 11 and Figure 12 show Bode diagrams of TiN and TiAlN/TiAlCrN coated Ti-6Al-4V alloy in 2 M NaOH, at 25 and 60 °C.

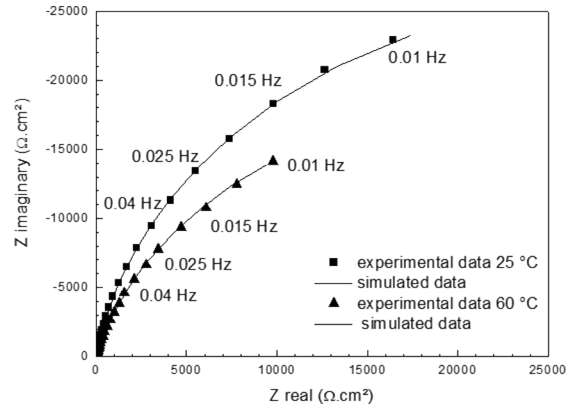


Figure 10. Nyquist diagram of TiAlN/TiAlCrN coated Ti-6Al-4V alloy in 2 M NaOH at 25 and 60 °C.

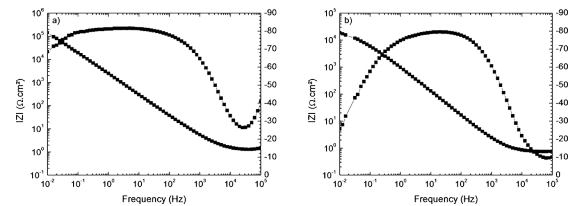


Figure 11. Bode diagrams of TiN coated Ti-6Al-4V alloy in 2 M NaOH: a) at 25, b) at 60 °C.

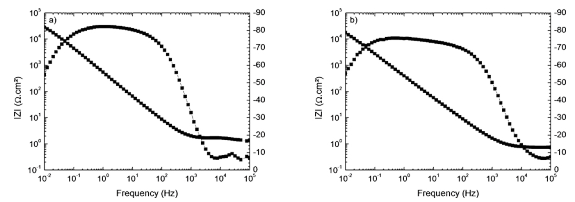


Figure 12. Bode diagrams of TiAlN/TiAlCrN coated Ti-6Al-4V alloy in 2 M NaOH: a) at 25, b) at 60 °C.

Table 2 shows the impedance parameters. They were calculated according to the adjustments made by the equivalent circuit model of two time constants for all experimental conditions.

Increasing temperature decreases the diameter of the semicircles that means decrease in the polarization resistance, i.e., lower corrosion resistance. Souza and Robin²⁸ in a study about concentration and temperature influence on the corrosion behavior of titanium alloys in sulfuric acid also observed a decrease of the semicircles of the Nyquist diagram with the increase of 25 °C for 50 °C.

Electrochemical impedance is a complex combination solution resistance of the interface capacitance, resistance to charge transfer and mass spectroscopy. At high frequencies the solution resistance predominates; while, at low frequencies, the charge transfer and mass becomes the main contribution to the impedance²⁹. In all solutions the alloy behaved according to the equivalent circuit model of two time constants. In corrosive process NaOH formed a dense film inner and a second one outer, but porous. According to Alves *et al.*²²,

Table 2. EIS data of uncoated, TiN, and TiAlN/TiAlCrN coated Ti-6Al-4V alloy obtained by equivalent electrical circuit models of two time constants.

Samples	Temperature (°C)	Parameters						
		CPE_p ($F.cm^{-2}$)	n_p	CPE_g ($F.cm^{-2}$)	n_g	R_s ($\Omega.cm^2$)	R_g ($\Omega.cm^2$)	R_p ($\Omega.cm^2$)
Ti-6Al-4V	25	8.7×10^{-5}	0.45	3.2×10^{-5}	0.91	0.91	189.0	4.4×10^4
	60	6.2×10^{-5}	0.92	1.1×10^{-4}	0.60	0.64	1.9	1.0×10^4
TiN	25	2.8×10^{-5}	0.76	5.0×10^{-5}	0.94	0.20	1.6	8.9×10^5
	60	6.2×10^{-5}	0.66	1.6×10^{-4}	0.90	0.77	0.8	2.3×10^4
TiAlN/TiAlCrN	25	1.0×10^{-6}	1.00	3.4×10^{-4}	0.90	1.33	0.3	6.0×10^4
	60	4.8×10^{-4}	0.84	5.8×10^{-5}	0.90	0.71	129.0	4.6×10^4

the layer that forms on the alloy Ti-6Al-4V is essentially TiO_2 , whether it is dense or porous.

The impedance results for all experimental conditions are in accordance with the potentiodynamic polarization, i.e., corrosion current density increasing (i_{corr}) means resistance to charge transfer (R_{ct}), or compact inner layer resistance (R_p) decreasing when temperature rises.

Analyzing the resistance of uncoated Ti-6Al-4V, R_p values are higher than R_g values. The inner dense layer controls the Ti-6Al-4V corrosion resistance. However, the R_g estimate the porosity degree of the outer layer. R_g higher values are related to less porous layers and vice versa²¹.

Table 3 summarizes electrochemical impedance values found in other studies about titanium corrosion behavior^{23,30-33}.

Table 3 shows that is very difficult to compare the impedance results with other authors as these results may vary in a wide range. Gheetha *et al.*³⁴ studied the influence of the microstructure and of alloying elements on corrosion behavior. They found different behaviors for different microstructures of a titanium alloy (Ti-13Nb-13Zr) in Ringer's solution. They observed that the quenched sample showed superior corrosion resistance due to uniform distribution of alloying elements in the different phases. The present work adopt an $\alpha + \beta$ alloy with lamellar microstructure, known as Widmanstätten morphology.

In the Bode diagrams, Z modulus or absolute impedance value ($|Z|$) and the phase angle (θ) is plotted against the frequency logarithm. If θ is equal to -90° , the electrode behaves as a capacitor; if θ equals 0° , the electrode behaves as a resistance. In general, in the regions at low and high

frequencies ($f < 10$ Hz or $f > 100$ kHz), the phase angle approaches to 0° . For intermediate frequencies ($0.1 < f < 100$ kHz) the phase angle remains close to -90° , indicating that the system resistance is controlled by surface polarizing of the working electrode. The higher is the range of intermediate frequency values close to -90° , more stable is the passivating film^{19,31}.

Ti-6Al-4V alloy showed nearly ideal capacitive behavior at the two studied temperatures (Figures 8, 11 and 12). Remaining in broad bands of intermediate frequency with a maximum phase angle close to -90° (at $25^\circ C \approx -80^\circ$; at $60^\circ C \approx -75^\circ$); and in $\log |Z| \times \log$ frequency plots, the slope is about -1. The results agree with other previous reports. Kumar *et al.*³⁵ and Wang *et al.*³⁶, who study Ti-6Al-4V electrochemical properties found $\log |Z| \times \log$ frequency plots slope close to -1 and the maximum phase angles between -70° and -85° .

The n values obtained from the $\log |Z| \times \log$ frequency slope ranged between $0.45 < n < 1.0$ and agrees with Grips *et al.*³⁷, Liu *et al.*³⁸ and Wan *et al.*³⁹ findings.

Alloying elements addition in binary nitrides of transition metals, such as Al and Cr, controls micropore size and density, improves the hardness and fracture toughness and increases corrosion and wear resistance³⁷. A multilayer coating improves corrosion behavior when compared with a simple coating because of the increased coating thickness, which leads to statistical decrease of defects possibility through the coating (pores). If a coating is composed of different structured layers, phases electrochemical potentials will be different. Thus, corrosion penetration towards substrate is

Table 3. EIS measurements of titanium alloys.

Referências	Meio de corrosão	Material	R (Ωcm^2)
MANHABOSCO <i>et al.</i> ²³	PBS	Ti-6Al-4V	1.4×10^6
BARRANCO <i>et al.</i> ³⁰	Hank	Ti-6Al-4V	1.5×10^7
VASILESCU <i>et al.</i> ³¹	Ringer	Ti-6Al-4V1Zr	5.2×10^5
CONTU <i>et al.</i> ³²	NaOH 2M	Ti-6Al-4V	6.5×10^3
DELGADO-ALVARADO <i>et al.</i> ³³	3,5 % p. NaCl	γ - TiAl	2.5×10^6

reduced due to current flow in the coating³⁸. However, in the present work, we observed that the multilayer E_{corr} values were slightly affected by differences in the microstructure of the layer. Furthermore, TiAlN/TiAlCrN coated Ti-6Al-4V alloy suffered spallation in all studied temperatures at the end of polarization test.

It is known that the aluminum atom concentration in the multilayer studied here is greater than the titanium concentration. According Grips *et al.*³⁷, Al concentration increasing lead to improved corrosion resistance. However, when Al concentration value is higher than 50 at. %, coating adhesion and hardness decrease. Kovalev *et al.*⁴⁰ reported a study about alloying elements addition impact on TiN mechanical properties. They concluded that both aluminum amount and defects percentage in microstructure influence coating stability. Grips and colleagues³⁷ informed that a multilayer prevents a direct path between the corrosive solution and the substrate, as an interlayer serves as a defects (micropores) block of the above one. In this present work, the blocking effect was negligible and allowed the corrosive solution reaching the substrate. Possible reasons, besides defects number increase by aluminum incorporation to nitride is: multilayer and interlayer thickness (total thickness = 6 μm , TiAlN = 540 nm, TiAlCrN = 217 nm) and interfaces number ($N = 11$). Results reported by Grips *et al.*³⁷, Liu *et al.*⁴¹ and Ananthakumar *et al.*⁴² showed good corrosion resistance results for multilayer coatings with a total thickness up to 2 μm , interlayer thickness of about 20-30 nm and interfaces number ranging from 45 <N <430.

Regardless the three studied conditions have different surfaces, E_{corr} , capacitance C , and exponential factor n values are similar (Tables 1, 2). This result can be explained based on the assumption that these measures are determined by TiO_2 thin film, which grown on each studied surface condition.²⁰

For a better understanding of the PVD surface treatment effects, we compare the results of uncoated, TiN and TiAlN/TiAlCrN coated Ti-6Al-4V alloy. The results were discussed in terms of protective efficiency and compared with corrosion tests that used other corrosion solutions.

Equation 4 calculates the efficiency of the protective coatings:

$$P_i(\%) = \left[1 - \left(\frac{i_{corr}}{i_{corr}^0} \right) \right] \times 10 \quad (4)$$

where i_{corr} is the corrosion current density at coated condition and i_{corr}^0 is the corrosion current density at uncoated condition⁴³.

Table 4 lists the coatings protective efficiency.

Based on Table 4 it can be seen that the TiN based coating showed better protective efficiency levels and offer better protection to the uncoated Ti-6Al-4V alloy.

Table 5 displays the main results obtained from Ti-6Al-4V corrosion tests in HCl⁹ and NaCl¹⁰.

Based on Table 5, a comparison between each condition gives an idea about the corrosion properties of Ti-6Al-4V

Table 4. Efficiency of the protective coatings in NaOH solution (%).

	TiN	TiAlN
25 °C	66	-
60 °C	41	41

alloy. At all conditions, increasing temperature decreased corrosion resistance. The corrosion resistance at uncoated and coated condition behaved as follows in each solution: NaCl > NaOH > HCl. The same analysis can be done based on coating type, thus, the corrosion behavior would alter as follows: TiN > TiAlN/TiAlCrN > uncoated Ti-6Al-4V alloy. But, some cases have singularities. First, at 25 °C, it is possible to see that i_{corr} hide the corrosion resistance variation between the solutions. This corrosion resistance difference appears on impedance measures. Second, in TiAlN/TiAlCrN coated condition at 25 °C, impedance measured in NaOH solution showed a lower value than impedance measured in HCl solution. According to Soliman⁴⁴, aluminum reacts with OH^- producing aluminate ion and providing higher corrosive activity. This could explain the lower corrosion resistance in NaOH solution that is less aggressive than HCl (once NaOH has no chloride ion and titanium behaves passively in alkaline medium). At last, in polarization test at 60 °C, i_{corr} measured in NaOH solution are slightly lower than i_{corr} measured in NaCl solution. This trend distinguishes from impedance analyses (impedance measured in NaOH solution are higher than impedance measured in NaCl solution). Increasing temperature favors localized corrosion through the coating pores or pitting formation on surface at uncoated condition. Localized corrosion increases current density and can affect i_{corr} measures. Impedance measure took place at corrosion potential, without disturbance and film destabilization, thus, give a more reliable result.

4. Conclusion

This paper concludes a series of analyzes about Ti-6Al-4V corrosion behavior treated superficially. The studies explore the behavioral corrosion titanium alloy, in different solutions, temperatures and coatings chemical compositions. This is an unpublished work that investigated the influence of microstructure, chemical reactions and temperature on the corrosion resistance of the alloy Ti-6Al-4V. The main conclusions were:

- impedance measures are more reliable than i_{corr} , once the later one gives a measure without disturbance;
- multilayers coating are, in general, more resistant than single coatings, but that rule change with the microstructure. Microstructural parameters like thickness, interlayers number and aluminum amount impact on coating corrosion behavior. The multilayer studied in the present work suffered spallation after polarization at all conditions studied;
- Increasing temperature favors pitting corrosion at uncoated condition and localized corrosion through the pores at coated conditions when chloride ions were present;

Table 5. Main results obtained from Ti-6Al-4V corrosion tests in HCl⁹ and NaCl¹⁰.

Temperature (°C)		Ti-6Al-4V	TiN	TiAlN
25	i_{corr} (A/cm ²)			
	HCl	10 ⁻⁵	10 ⁻⁷	10 ⁻⁷
	NaOH	10 ⁻⁷	10 ⁻⁷	10 ⁻⁷
	NaCl	10 ⁻⁷	10 ⁻⁷	10 ⁻⁷
	R (Ω.cm ²)			
	HCl	10 ³	4.7x10 ⁵	10 ⁵
	NaOH	10 ⁴	8.9x10 ⁵	10 ⁴
	NaCl	10 ⁵	10 ⁷	10 ⁷
	60	i_{corr} (A/cm ²)		
HCl		10 ⁻⁴	2.4x10 ⁻⁶	2.5x10 ⁻⁶
NaOH		2.2x10 ⁻⁶	1.3x10 ⁻⁶	1.3x10 ⁻⁶
NaCl		3.7x10 ⁻⁶	2.0x10 ⁻⁶	1.4x10 ⁻⁶
R (Ω.cm ²)				
HCl		-	-	-
NaOH		10 ⁴	10 ⁴	10 ⁴
NaCl		10 ⁵	10 ⁶	10 ⁶

- Increasing temperature decreases corrosion resistance at all studied conditions.

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