



Electrodeposition of polypyrrole onto NiTi and the corrosion behaviour of the coated alloy

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ABSTRACT

Polypyrrole (PPy) films were electrodeposited onto nickel–titanium alloy (NiTi) employing sodium bis(2-ethylhexyl) sulfosuccinate (Aerosol OT or AOT) solutions. Polarizing anodically NiTi samples recovered by PPy in a monomer-free solution increases adhesion of the coating. Electrochemical techniques, scanning electron microscopy (SEM) and element analysis were used in determining the corrosion performance of the coated samples in chloride solution. The polymer improves the corrosion performance at the open circuit potential and at potentials where the bare substrate suffers pitting attack. The improvement in both, adhesion and corrosion performance, is discussed considering substrate/polymer interaction, overoxidation of PPy and the role played by AOT.

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1. Introduction

Titanium and its alloys are widely used in clinical applications because their excellent corrosion resistance and biocompatibility. The corrosion resistance is the result of the formation of a thin passive TiO₂ films on the metal surface. Among others Ti-alloys, nearly equiatomic NiTi has been extensively used in medical and dental applications, being its principal use in the field of self-expanding vascular and non-vascular stents. The main problem connected with using NiTi is the release of Ti and Ni ions into the biological environment [1–3]. According to the literature, pitting can be observed on NiTi surfaces under anodic polarization in chloride-containing aqueous solutions [2,4–7]. Chemical passivation [2], surface modification techniques such as laser welding treatment [4], laser melting surface [6], ion implantation [8] and thermal treatment [9] have been used to improve the corrosion resistance of titanium alloys.

In recent years there has been an increased interest in the use of conducting polymers as protective coatings against corrosion. Polypyrrole is particularly attractive due to its high stability and relatively simple preparation in aqueous solutions. In addition, PPy exhibits very good tissue compatibility *in vitro* and *in vivo* [10]. Thus, Ti-based materials coated by PPy present important advantages for biomedical applications. The polymer could be modified by biologically active molecules and at the same time, it could act as an anti-corrosion coating.

In our laboratory we have successfully electropolymerized pyrrole at Fe and Al from a solution containing sodium bis(2-ethylhexyl) sulfosuccinate (Aerosol OT or AOT) [11,12]. These films have significant corrosion protection properties in chloride solution because AOT is a bulky anionic surfactant that remains entrapped in the polymer matrix, inhibiting the anion exchange between the polymer and the electrolyte solution. In addition, the monomer is solubilized and concentrated in the micellar assembly of surfactant molecules formed on the substrate surface. As a result the deposition rate is increased and the polymer is formed by very small grains. Smoother and more compact morphologies were obtained compared to those synthesized with inorganic anions.

In this work the first results of research aimed to obtain adherent and protective PPy coatings onto NiTi alloy are presented.

2. Material and methods

Electrodes were prepared from NiTi alloy (Ni: 55.8 wt.%, O: 0.05 wt.%, C: 0.02 wt.%, Ti: balance) rod samples. The rods were embedded in a Teflon holder with an exposed area of 0.070 cm². Before each experiment, the exposed surfaces were polished to a 1000 grit finish using SiC, then degreased with acetone and washed with triply distilled water. Following this pretreatment, the electrode was immediately transferred to the electrochemical cell. All the potentials were measured against a saturated calomel electrode (SCE) and a platinum sheet was used as a counter electrode. The cell was a 20 cm³ Metrohm measuring cell.

The PPy films were synthesized electrochemically onto NiTi alloy from a 0.05 M AOT solution of pH 7 containing 0.25 M pyrrole

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(Py) using three methods. In the first procedure, the working electrode potential was cycled between -1.0 and 1.0 V(SCE) at a scan rate of 50 mV/s, while in the second and the third procedure the electrode was maintained under galvanostatic (15 mA/cm²) and potentiostatic (0.9 V(SCE)) conditions, respectively. The corrosion behaviour of NiTi and NiTi coated with PPy was analyzed in 0.15 M NaCl solution. The cell was purged with nitrogen gas saturated atmosphere at 25 °C in the majority of experiences.

Electrochemical measurements were done using a potentiostat–galvanostat PAR Model 273A and electrochemical impedance spectroscopy (EIS) experiments were carried out by means of potentiostat–galvanostat Voltalab 40 Model PGZ 301. Ac impedance spectra were recorded at a fixed potential (0.65 V(SCE)) using an excitation voltage of 10 mV. The frequency range studied was between 10 kHz and 10 mHz.

ISI DS 130 SEM was used to examine the electrode surface characteristics. Ni and Ti concentrations in chloride solution from NiTi alloy were determined using inductively coupled plasma atomic emission spectrometry (ICP-AES).

Adhesion of PPy film synthesized onto NiTi alloy was tested using Scotch[®] Magic[™] Tape 810 (3 M). PPy surface was always washed with triply distilled water and dried in stream of nitrogen prior to test. A piece of adhesive tape was pressed to the PPy film and pulled off. It was checked if the film was not at all removed, removed in patches, or completely removed.

All chemicals were reagent grade and solutions were made in triply distilled water. Pyrrole was purchased from Sigma–Aldrich and it was freshly distilled under reduced pressure before use. The surfactant AOT was purchased from Alfa Aesar. In order to avoid the slow hydrolysis of AOT all the measurements were done with freshly prepared samples.

3. Results and discussion

3.1. Electrochemical synthesis

In an attempt to produce electropolymerization of PPy onto NiTi, potentiodynamic, galvanostatic and potentiostatic polarizations were carried out in 0.05 M AOT solution of pH 7 with 0.25 M Py (Figs. 1–3). Polymer growth can be achieved by employing all these techniques. The electrochemical responses of NiTi in 0.05 M AOT monomer-free solution are also included in the figures.

The potentiodynamic polarization of NiTi alloy in the monomer-free pH 7 solution (Fig. 1A) shows an active/transition process followed by a current increase related to transpassive dissolution of the NiTi alloy [13]. The anodic current decreases markedly in the second cycle, indicating a complete passivation of the NiTi electrode. It was reported that the thin passive film consists primarily of Ti(IV) oxide and Ni(II) oxide with some enrichment of Ni at the interface between the oxide and the metal [2].

The first cycle in the AOT solution containing the monomer (Fig. 1B) presents an increase in the anodic current density at about 0.5 V(SCE), which corresponds to Py oxidation. The current loop in the following negative scan is associated with the nucleation and growth of the polymer [14]. New oxidation–reduction waves appear whose charges increase with subsequent sweeping indicating the build-up of polymeric products. A uniform and homogeneous PPy film was obtained after the potentiodynamic polarization.

When a constant anodic current density is applied in the absence of the monomer the potential attained very high values (Fig. 2, curve a) leading to the growth of a blue-violet film, probably Ti₂O₃ or Ti₃O₅ [15]. The galvanostatic response obtained with Py shows a potential increase in a first stage and then the potential reaches a stable plateau where PPy electrodeposition occurs (Fig. 2, curve b).

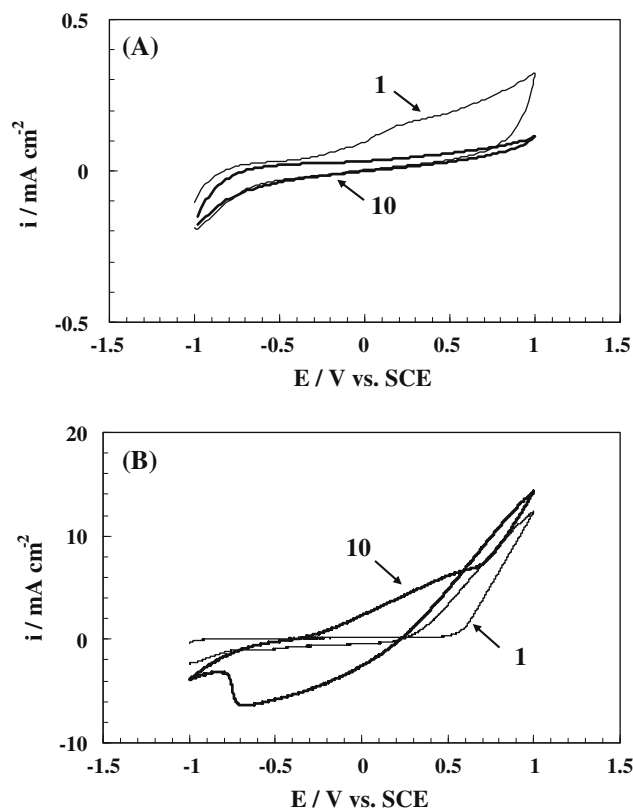


Fig. 1. Potentiodynamic polarization obtained for a NiTi electrode in 0.05 M AOT, pH 7 solution: (A) without Py and (B) with 0.25 M Py. The cycle numbers are indicated. Scan rate: 0.05 V/s.

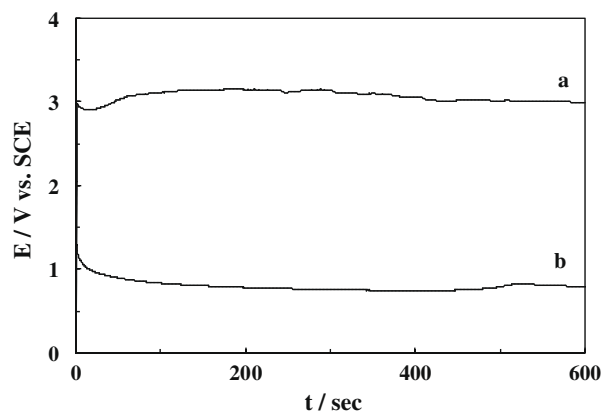


Fig. 2. Galvanostatic response obtained at 15 mA/cm² for a NiTi electrode in 0.05 M AOT, pH 7 solution: (a) without Py and (b) with 0.25 M Py.

The potentiostatic response obtained without the monomer shows a current decrease associated with the formation of the oxide layer (Fig. 3, curve a). The current decay is associated with a decrease of field strength as the oxide film thickens [16].

Conversely, the current transient recorded in the presence of the monomer shows that, after a very short time (0.5 s), the current increases leading to the growth of the polymer film (Fig. 3, curve b).

3.2. Adherence of PPy films

The obtained PPy film can be easily removed from the substrate, independently of their thickness and the electrosynthesis technique employed. When using titanium as a substrate very poor

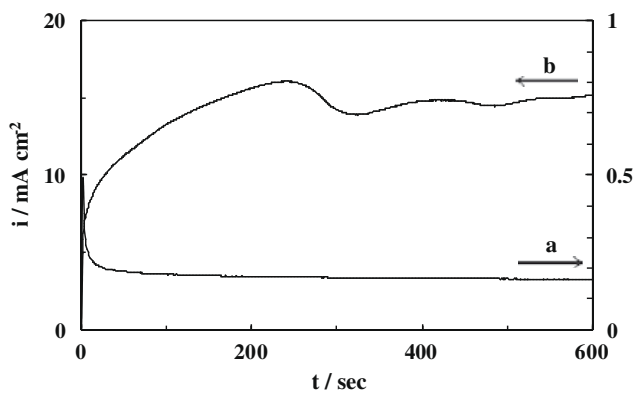


Fig. 3. Potentiostatic response obtained for a NiTi electrode in 0.05 M AOT, pH 7 solution after application a potential step from 0.0 to 0.9 V(SCE): (a) without Py and (b) with 0.25 M Py.

adhesion was observed for the polymer grown over the native oxide [17]. On the other hand, it was proposed that dissolution of Ni occurs simultaneously with deposition of PPy when the electropolymerization was done onto a Ni electrode [18]. Deposition of the polymer film hinders further Ni dissolution and then the PPy film on the metal surface can be grown. It was also supposed that during the formation of PPy on Ni electrode, complex compounds of $\text{Ni}^{2+}\text{-xPy}$ rings are formed and that these compounds are part of the film. Then, it is expected that the electropolymerization will be more complex in the case of NiTi alloy as a substrate because anodic polarization would result not only in PPy deposition but also in Ni dissolution. The later processes could affect adhesion of the film.

Further experiments were made in order to improve the film adhesion to the NiTi surface. The best results were obtained when a PPy film formed at 0.9 V(SCE) during 1800 s in 0.05 M AOT solution of pH 7 with 0.25 M Py was anodically polarized in AOT monomer-free solution. A thickness of approximately 90 μm is predicted for the coating by assuming a film thickness of 1 μm for 0.4 C/cm^2 charge [19].

Applied potential and polarization time in the monomer-free solution were varied in order to find the optimum adhesion of the coatings. It was found that the minimum applied potential required to obtain good adhesion is 1.0 V(SCE). Moreover, for a fixed potential, the attained adhesion depends on the potentiostatization time. By applying 1.0 V(SCE), no adhesion was observed after 120 s of polarization, while 300 s provides partial adhesion to the substrate. Finally, if the PPy-coated electrode was polarized during 600 s the film cannot be removed by the scotch tape. Thus, adhesion to the substrate depends on applied potential and polarization time.

The applied anodic polarization seems necessary to the formation of a proper composite material PPy/oxide which increases remarkably the polymer adherence. As a result of the treatment, penetration of the solvent into the polymer matrix allows oxide growth to be the main reaction at the substrate/polymer interface. Moreover, overoxidation of the polymer can take place in this potential region. It was reported the synthesis of well-adhering overoxidized PPy films onto active metals [20]. In order to check if overoxidation occurs, the redox behaviour of a treated sample was analyzed in pure AOT solution by potentiodynamic polarization. Considering that the potentiodynamic curve for PPy electro-synthesized under high deposition charges is practically a straight line (resistive response), a film deposited at 0.9 V(SCE) during a short time (120 s) was analyzed. It was found that the treatment caused a loss of electrochemical activity, indicating that the film was irreversibly overoxidized.

3.3. Corrosion behaviour

The corrosion behaviour in chloride solution of the bare sample and the PPy-coated alloy submitted to anodic polarization in a monomer-free solution was analyzed.

Fig. 4 displays the open circuit potential (OCP) of NiTi alloy with and without PPy coating in 0.15 M NaCl solution as a function of time. As seen, the potential of the uncoated electrode (Fig. 4, curve a) shifts towards less negative values in the first seconds of immersion and then shows a constant value of -0.230 V(SCE). This indicates the formation of a passive oxide film on the alloy surface [3]. On the other hand, the potential of coated NiTi (Fig. 4, curve b) moves smoothly in the negative direction reaching a constant value of 0.041 V(SCE). Thus, the OCP of coated NiTi is about 0.190 V higher than that of uncoated one.

The Tafel plots for the coated and uncoated electrodes in deaerated 0.15 M NaCl solution are presented in Fig. 5. The samples exhibit the same anodic polarization behaviour but the coated alloy has a higher rate of reduction reactions in comparison with the bare material. No major differences were observed in the polarization curve for the coated electrode when the solution was aerated. These results can be interpreted considering that the reduction reaction of the polymer significantly contributes to the total cathodic current measured. Potentiostatic curves registered at -0.15 and -0.25 V(SCE) showed that the current decayed monotonically with time until a steady state was reached. It is an expected result if the polymer reduction reaction takes place. Thus, the higher anodic current measured at the OCP not necessarily imply a higher corrosion current as reported by other workers [21–25]. It should be considered that redox phenomena of the polymer occur simultaneously with the corrosion reaction. It was postulated that galvanic coupling of the polymer to the substrate should contribute to oxidize the substrate forming a passive film.

The corrosion performance of the PPy-coated NiTi electrode was analyzed by comparing the total Ni and Ti quantity released from coated and uncoated alloys under OCP conditions in 0.15 M NaCl solution during 170 h. The concentrations of Ni and Ti in solution for the bare NiTi were 0.61 and less than 0.05 mg/L, respectively. The quantity released of Ni and Ti in the case of the coated sample was 0.32 and less than 0.05 mg/L, respectively. Thus, the concentration of Ni was reduced to half when the alloy was coated with the PPy film, corroborating that the interaction between the substrate and the polymer is effective in inhibiting corrosion.

The anodic polarization curve of NiTi in 0.15 M NaCl solution (Fig. 6, curve a) is characterized by a passive region (extending from the OCP) being TiO_2 the main component of the passive film

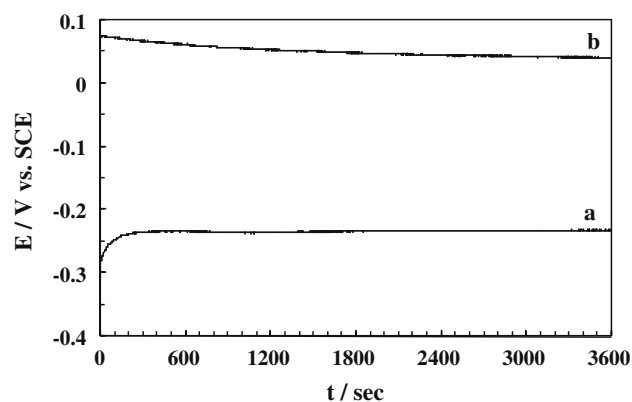


Fig. 4. Open circuit potential (OCP) vs. time plot in 0.15 M NaCl solution for: (a) uncoated NiTi and (b) PPy-coated NiTi. The polymer was synthesized at 0.9 V(SCE) during 1800 s in 0.05 M AOT + 0.25 M Py solution, pH 7.

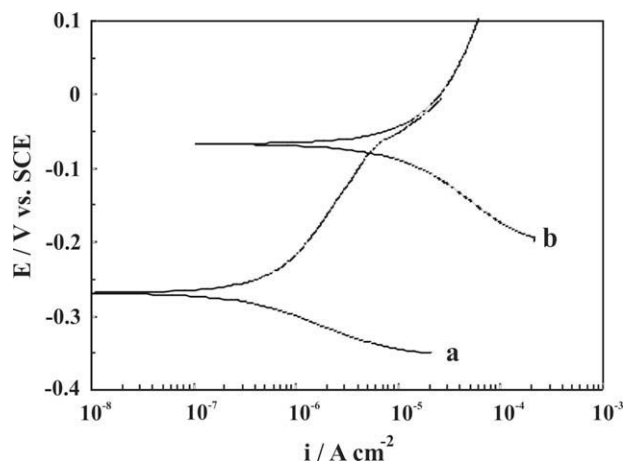


Fig. 5. Tafel curves registered after OCP measurements in 0.15 M NaCl solution at 0.001 V/s for: (a) uncoated NiTi and (b) PPy-coated NiTi.

[2]. An increase in the current density is recorded above approximately 0.30 V(SCE), indicating breakdown of passivity. This measured breakdown potential is in accordance with values reported previously [7].

In order to avoid crevice corrosion, a NiTi sample was not embedded in the Teflon holder and only the circular area of the cylinder was exposed to the electrolyte solution. This electrode has the same polarization behaviour as the embedded alloy, indicating that the increase in current density produced around 0.3 V(SCE) is related to the initiation and propagation of pits.

The anodic current density registered for the PPy-coated electrode (Fig. 6, curve b) is related to the oxidation of the polymer itself, while overoxidation and oxidation of the medium occur at the more positive potentials. Current peaks associated with polymer oxidation are better seen in the insert of Fig. 6.

The current density–time curve registered at 0.65 V(SCE) for the uncoated alloy is presented in Fig. 7. SEM micrograph of the electrode surface after 1800 s of polarization indicates localized corrosion of the sample (Fig. 8).

The anodic current measured for the coated sample polarized at 0.65 V(SCE) was significantly smaller than that for the bare alloy even after 12 h of polarization (Fig. 9). The current registered during this period for electrodes submitted and not submitted to anodic polarization in monomer-free solution before immersion in the chloride solution are compared in the figure. Current spikes

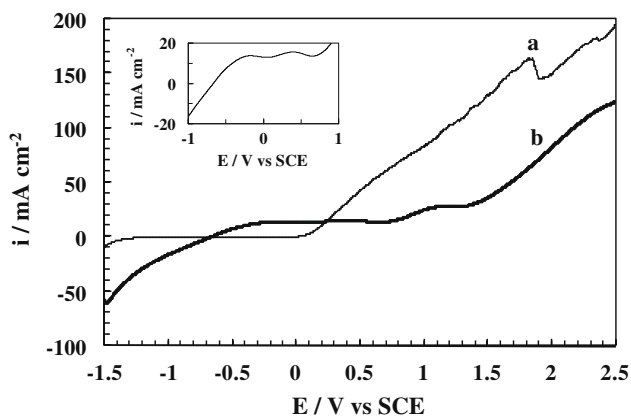


Fig. 6. Polarization curves registered in 0.15 M NaCl solution at 0.050 V/s for: (a) uncoated NiTi and (b) PPy-coated NiTi. Small inset: amplified zone of the polarization curve for the coated sample.

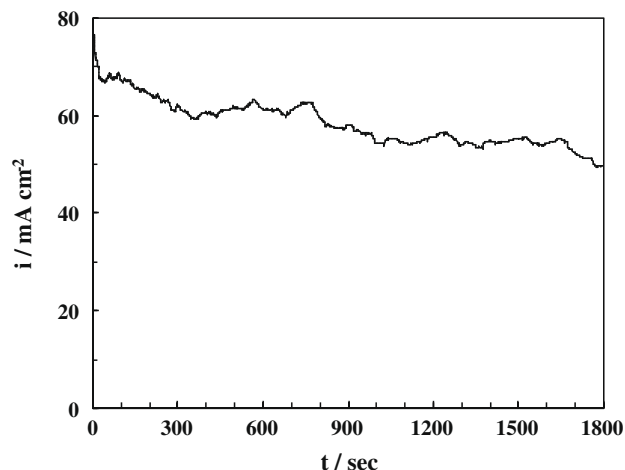


Fig. 7. Potentiostatic response obtained for an uncoated NiTi at 0.65 V(SCE) in 0.15 M NaCl solution.

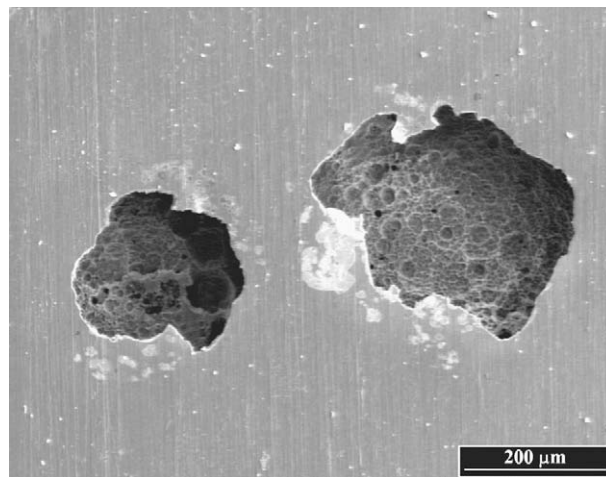


Fig. 8. SEM micrograph of the uncoated NiTi electrode after 1800 s of polarization at 0.65 V(SCE) in 0.15 M NaCl solution.

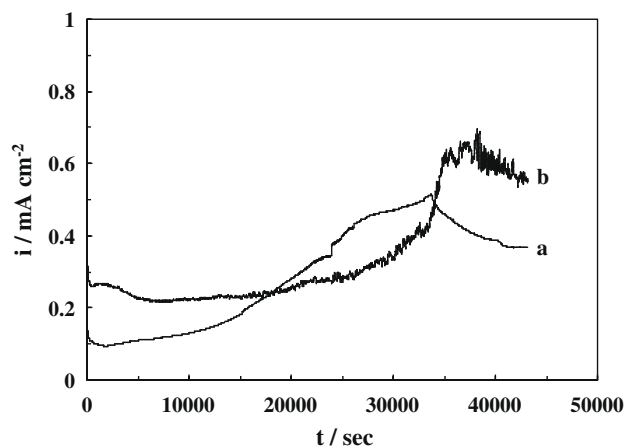


Fig. 9. Potentiostatic response obtained for a PPy-coated NiTi at 0.65 V(SCE) in 0.15 M NaCl solution: (a) submitted and (b) not submitted to anodic polarization (1 V(SCE)) during 600 s) in 0.05 M AOT monomer-free solution.

of current are observed in the case of the sample not submitted to overoxidation, indicating initiation and repassivation of metastable

pits. The treated sample presents a higher resistance to pitting attack considering that current fluctuations are almost imperceptible. At this potential (0.65 V(SCE)) dissolution of the substrate to form oxide is probably the main process at the electrode surface. The rate of the process decreases with polarization time.

On the other hand, the coated electrode was examined after polarization at 0.65 V(SCE) using SEM (Fig. 10). The absence of any detectable change in the polymer surface indicates no occurrence of pitting corrosion after 12 h of polarization at 0.65 V(SCE).

The concentrations released of Ni and Ti at 0.65 V(SCE) in chloride solution, were also analyzed. For the uncoated NiTi electrode, the polarization during 1800 s produced a concentration of Ni and Ti in solution of 14.96 and 4.41 mg/L, respectively. The release of Ni and Ti decreases significantly for the coated sample even after a longer polarization time. The quantity released of Ni and Ti after 12 h of polarization was 2.23 and 0.10 mg/L, respectively. The obtained results confirm that the PPy film potentiostatically formed onto NiTi alloy and anodically polarized in a monomer-free solution offers protection to localized corrosion in aggressive media.

The corrosion resistance of the coated and uncoated samples polarized at 0.65 V(SCE) in chloride solution was also evaluated by EIS (Fig. 11). Although detailed analysis of the spectra is not attempted here, it can be observed that the magnitude of the impedance notably increases when the NiTi alloy is covered by PPy film. The total impedance for the uncoated alloy after 2 h of polarization is 0.026 k Ω cm² (Fig. 11A) while the value corresponding to the PPy-coated sample is 1.4 k Ω cm² (Fig. 11B, curve a). The lower impedance of the bare alloy is the result of breakdown of the passive film followed by pits growth.

The Nyquist plot for PPy-coated alloy exhibits a depressed semi-circle. The magnitude of the impedance remains almost unchanged even after 12 h of polarization (Fig. 11B, curve b), which can be explained by the fact that the impedance spectra are dominated by the properties of the oxide and polymer films. In general, the existence of only one semicircle over the whole frequency range in impedance plot indicates no deterioration of the film. In contrast, polymer breakdown give rise of significant differences in the impedance spectra, generally the appearance at low frequencies of a second semicircle associated with the metal/electrolyte interface [26].

The above results also confirm that the anodic current measured for the PPy-coated NiTi at potentials where the bare alloy undergoes pitting is likely to be due to the response of the polymer and not to breakdown of the oxide (Fig. 6, curve b). The protection

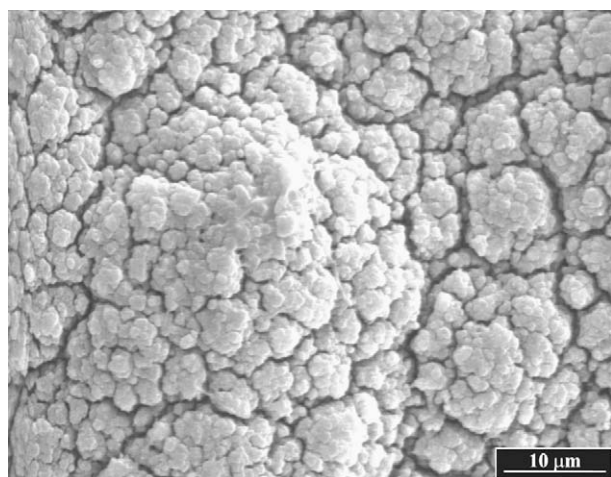


Fig. 10. SEM micrograph of coated NiTi electrode after 12 h of polarization at 0.65 V(SCE) in 0.15 M NaCl solution.

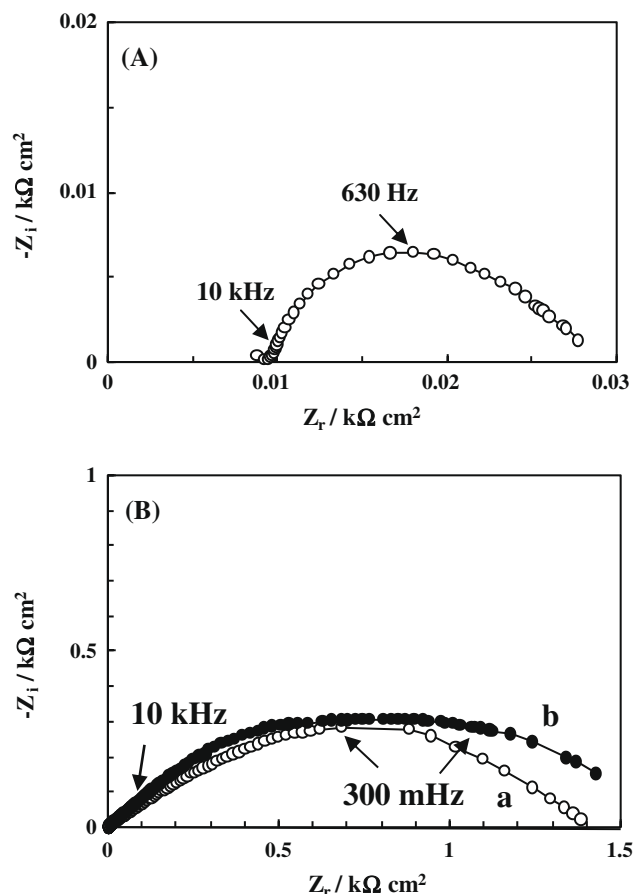


Fig. 11. (A) Nyquist plot for uncoated NiTi registered at 0.65 V(SCE) in 0.15 M NaCl solution after 2 h of polarization, and (B) Nyquist plots for PPy-coated NiTi registered at 0.65 V(SCE) in 0.15 M NaCl solution after: (a) 2 and (b) 12 h of polarization.

from localized corrosion is due to the incorporation of AOT molecules in the polymer matrix. Previous results indicate that an AOT molecules acts as an immobilized dopant when the PPy films is synthesized onto Al and Fe electrode [11,12]. On the other hand, considering the positive applied potentials and the permeation of water through the polymer matrix, the passive oxide film can be replenished by oxidation of the substrate, minimizing the rate of localized attack.

Contrary to pure Ti and Ti4Al6V medical alloys, which easily repassivate after surface damage, the NiTi oxides have a lower resistance to localized attack [27]. The bare NiTi alloy has a pitting potential relatively low to be used for implants in the human body. Then the higher resistance to localized attack of the PPy-coated NiTi alloy is a promising result.

4. Conclusions

The electrodeposition of PPy onto NiTi alloy was successfully carried out in a neutral AOT solution using potentiodynamic, potentiostatic and galvanostatic techniques. The obtained coatings were uniform and compact but their adhesion to the substrate surface was poor. Adherence of the coating was strongly improved when the electrode coated with a potentiostatically synthesized film was submitted to an anodic polarization in a monomer-free solution. The probably causes for this improvement are considered to be the formation of a composite material PPy/oxide and overoxidation of the polymer film.

The coating is able to retard the corrosion of the substrate under OCP conditions in chloride solution. This result is explained considering the low mobility of the AOT in the polymer matrix and the stabilization of the oxide film through interaction between the PPy and the underlying alloy. It was found that the NiTi surface was pitted at potentials higher than 0.30 V(SCE). The polymer coating presents also the ability to protect NiTi against localized corrosion. The higher corrosion resistance points out the important role that plays AOT as a dopant. The result is interpreted taking also into account the stabilization of the oxide film by a substrate/polymer interaction at these positive potentials and overoxidation of the polymer.

Acknowledgments

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