Low-Voltage Polarization in AOT Solution to Enhance the Corrosion Resistance of Nitinol

Melisa Saugo, Daniel O. Flamini, and Silvana B. Saidman

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In this work, the corrosion behavior of bare nitinol (NiTi) alloy in Ringer's solution containing different concentrations of sodium bis(2-ethylhexyl) sulfosuccinate (AOT) was first studied in order to determine whether the surfactant acts as a corrosion inhibitor. Results of potentiostatic and potentiodynamic experiments allowed concluding that AOT is a pitting corrosion inhibitor for NiTi. In a second stage of this research work, NiTi was treated under potentiostatic control (2.00 V) for 1 h in 0.10 M AOT solutions of pH 8.4 and 12. Static and rotating electrodes were used. The influence exerted by this treatment on the passive behavior of the alloy was studied in Ringer's solution using different electrochemical and surface analysis techniques. The best anticorrosion performance was obtained using a rotating electrode and AOT solution of pH 8.4. The thin oxide layer grown potentiostatically consists of TiO_2 , while no Ni was found in the outermost layer. The presence of this oxide layer allows reducing the amount of Ni and Ti released at open circuit potential conditions and at very positive potentials where pitting corrosion of the bare alloy occurs.

Keywords AOT, corrosion inhibition, low-voltage polarization, nitinol

1. Introduction

Among titanium-based alloys, nitinol (nearly equiatomic Ni and Ti alloy (NiTi)) has the highest amount of applications in the biomedical industry due to a combination of mechanical properties, such as shape memory and superelasticity, and physicochemical characteristics, including biocompatibility (Ref 1). Furthermore, NiTi alloy has good corrosion resistance due to the spontaneous formation of an oxide film composed mainly of TiO_2 (Ref 2). However, the high Ni content in the alloy can lead to the release of Ni^{2+} ions into the human body, which can cause toxic, allergic or carcinogenic effects (Ref 3). Then, it is necessary to modify the surface of the alloy in order to improve its corrosion resistance and biocompatibility which is one of the most important requirements when NiTi is used as biomaterial. In this sense, many authors have devoted their effort to modify the surface through the use of different techniques, such as heat treatments (Ref 4), chemical etching (Ref 2), laser irradiation (Ref 5, 6), and plasma immersion ion implantation (Ref 7).

The anodization method is also a surface modification technique that improves the corrosion resistance. Only the metals classified as valve metals are capable of forming an oxide layer through this method (Ref 8). Titanium is a valve metal and its electrochemical anodization has been extensively

studied (Ref 9, 10). Anodic polarization in an appropriate electrolyte leads to the growth of an oxide film on the substrate surface. Under galvanostatic control, thickening of the oxide film is accompanied by a significant potential shift. The addition of a high concentration of an alloying element, which is not a valve metal, inhibits the growth of the oxide layer (Ref 8). This is the case of NiTi, where thinner films were formed and the voltage increase was always much smaller than for pure Ti (Ref 8, 11, 12). However, a thin corrosion protective film was formed on NiTi by anodic polarization in acetic acid solution (Ref 11). Galvanostatic anodization in Na_2SO_4 solution leads to the formation of an oxide film with a Ni-free surface zone which blocks the release of Ni ions in simulated body fluids (Ref 13). A Ni-free oxide was also obtained by anodic polarization in nitric acid solution (Ref 8). In this case, the simultaneous release of Ni during the oxide growth generated pits in the oxide layer.

A low-voltage method in the presence of molybdate solutions was employed recently in our laboratory as an alternative process to protect NiTi alloy from pitting corrosion in Ringer's solution (Ref 12). The oxide formed potentiostatically consisted mainly of TiO_2 with a small trace of nickel, and the mole ratio Ti/Ni on the outermost surface of the oxide was considerably increased. The increase in TiO_2 content on the surface, which formed a new, stable and defect-free protective layer, resulted in an improvement in the corrosion behavior. The presence of molybdenum species in the oxide layer also contributed to the corrosion resistance improvement.

It is known that the molecules of different surfactants can be adsorbed on metal surfaces and act as corrosion inhibitors (Ref 14–16). At very low concentration, there is only a slight adsorption of surfactants on the substrate (Ref 16). As the concentration increases, the molecules adsorb on the metal and cover the surface forming a monolayer, relatively uniform and porous with rather good corrosion protection properties. With a further increase in the surfactant concentration, up to and beyond the critical micelle concentration (CMC), the growth of aggregates on the substrate occurs mainly by bilayers/multilayers adsorption. The monolayer level is sufficient for

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significant inhibition. Hence, the changes above the CMC result only in additional coverage beyond the monolayer, which leads to small changes in inhibition (Ref 17, 18). Sodium bis(2-ethylhexyl) sulfosuccinate (AOT) is a bulky anionic surfactant widely used to form reverse micelles. The molecule has two large-branched alkyl chains and a sulfonate head group. As was previously demonstrated by Branzoi et al. (Ref 19), the presence of an anionic surfactant such as AOT exerted a great inhibitory effect on carbon steel corrosion in sulfuric acid medium. AOT was formerly used in our laboratory as a dopant when polypyrrole (PPy) films were deposited on Ti. The AOT molecule acted as an immobilized dopant, providing a higher corrosion resistance to the PPy coating (Ref 20).

The first objective of this research work is to demonstrate whether the addition of a surfactant such as AOT shows any inhibitory effect on the pitting corrosion of NiTi alloy in Ringer's solution. As a second objective, a low-voltage polarization technique was used in the presence of AOT in order to grow an oxide layer on the NiTi alloy surface. This method can be considered as an alternative to protect the alloy from corrosion.

2. Materials and Methods

NiTi rods axially mounted in a Teflon holder were used as working electrodes (WE). The exposed area of the WE is 0.0962 cm^2 , and its chemical composition (in wt.%) is: 55.8 Ni, 0.05 O, 0.02 C and Ti balance. Before each experiment, the WE was abraded with SiC papers down to a 1200 grit finish, then degreased with acetone, and finally washed with triply distilled water. A large Pt sheet was used as counter electrode, and a saturated calomel electrode (SCE) was used as reference electrode. All potential values in this work are referred to SCE. All electrochemical experiments were performed in a Metrohm cell of 20 cm^3 utilizing a potentiostat–galvanostat AUTOLAB/PGSTAT128N (Eco Chemie, the Netherlands).

Anodic polarization of NiTi alloy was carried out potentiostatically using a static electrode and a rotating disk electrode EDI 101 with a CTV 101 rotation rate controller (Radiometer Analytical S.A.) in 10^{-1} M AOT solutions. The samples were prepared using AOT solutions of different pH values: 8.4 (as-prepared) and 12 (adjusted by adding NaOH). The different samples will be named as $\text{NiTi}_{8.4}$, $\text{NiTi}_{8.4\omega}$, NiTi_{12} , and $\text{NiTi}_{12\omega}$, where the subscript indicates the pH and the use of a rotating electrode (ω).

The inhibitory effect of AOT and the corrosion performance of the anodically polarized surfaces were evaluated in Ringer's solution (0.147 M NaCl ; 0.00432 M CaCl_2 ; 0.00404 M KCl , giving a total chloride concentration of 0.16 M). All chemicals were of reagent grade, and solutions were made with triply distilled water. The electrochemical techniques to determine the corrosion performance included the registration of the open circuit potential (OCP) variation with time for one week, linear sweep voltammetry (LSV), where the potential was swept from -0.50 V at a 1 mV s^{-1} rate, and potentiostatic measurements, where a potential of 0.65 V was applied during 12 h. Tafel plots were also registered, and in this experiment, the potential was swept at 1 mV s^{-1} from -0.20 to $+0.20 \text{ V}$ versus OCP.

Ni and Ti released concentrations in Ringer's solution were analyzed using an inductively coupled plasma atomic emission spectrometer (ICP-AES) (ICPE 9000, Shimadzu Corporation,

Japan). A LEO 1450 VP scanning electron microscopy (SEM) coupled with a probe for energy-dispersive scanning (EDX) was used to examine the characteristics of the electrodes surface. To determine the roughness of the samples, a contact atomic force microscope (AFM) in air commanded by a Nanoscope IIIa control unit from Veeco Instruments was employed, with commercial SiN probes and typical forces in the range of $50\text{--}220 \text{ nN}$. XPS analysis was carried out on a Multitechnical Specs equipped with a dual x-ray source (Mg/Al), a monochrome dual x-ray source (Al/Ag), and a hemispheric analyzer (PHOIBOS 150) in Fixed Analyzer Transmission (FAT) mode. The spectra were obtained with a pass energy of 30 eV and Al and/or Mg anode operated at 150 W according to technical requirements. The pressure during the measurement was less than $2 \times 10^{-9} \text{ mbar}$. The samples (1 cm^2) were supported on the sample holder using double-sided copper tape and then evacuated to ultrahigh vacuum for at least 12 h before readings. The energies of all spectra were referenced to the C 1s peak at 285.0 eV . All the XPS spectra were deconvoluted using CasaXPS software with a Gaussian–Lorentzian mix function. Contact angle measurements of the samples were performed in order to characterize the hydrophobic or hydrophilic nature of the surfaces. The measurements were performed at 25°C using a $5 \mu\text{L}$ droplet of triply distilled water and an optical contact angle (OCA 20) system (DataPhysics Instruments GmbH, Germany). The values reported in this work are the average of three measurements taken after 30 s of stabilization on the substrate surface.

3. Results and Discussion

3.1 AOT as Corrosion Inhibitor

As it was stated before, the use of surfactants as metal corrosion inhibitors is a widely studied subject. However, the employment of surfactants to inhibit the corrosion of NiTi alloy is not so much. To determine whether the AOT acts as a corrosion inhibitor for NiTi, different experiments were performed in Ringer's solution.

NiTi alloy has a relatively low pitting potential in chloride solution (Ref 21). With the purpose of finding out whether the addition of AOT results in a shift in the pitting potential, a LSV of the bare alloy was performed in Ringer's solution containing different AOT concentrations (from 10^{-3} to 10^{-1} M) (Fig. 1). When AOT is present, there is a positive shift in the pitting potential for every one of the samples. It can be seen that for higher concentrations, after the pitting process has begun, the current density suddenly falls until it reaches a value close to zero again (Fig 1, curves c and d). Then, after 1.5 V , the current density rises again. This last increment is related to oxygen and chlorine evolution reactions (Ref 22, 23). The values for the pitting potentials obtained in the presence of the different AOT concentrations are presented in Table 1.

It should be noticed that AOT's CMC in water is $2 \times 10^{-3} \text{ M}$ (Ref 24), which means that the decrease in current density is observed when the AOT concentration is higher than the CMC (10^{-2} and 10^{-1} M). In both cases, white corrosion products were seen covering part of the electrodes when they were removed from the electrochemical cell. When the electrodes were washed and the corrosion products removed, pits were detected on the surface of the bare alloy. The fact that

the corrosion products were covering the pits could explain the current density decrease observed in Fig. 1, curves c and d. Figure 2 shows a SEM image of one of the pits formed during the experiment. Letters A and B show the points where EDX spectra were taken, and their quantitative analyses are presented in the inset table. These spectra determined the presence of S and Cl inside the pit (Fig. 2, point A) but not outside of it (Fig. 2, point B). This could indicate that, during the pitting of the bare alloy, the interaction between the AOT molecules and the alloy surface might be different inside and outside the pit.

In order to ensure that the current density increment and decrease during the potentiodynamic polarization curves (Fig. 1, curves c and d) are due to the pitting corrosion of the substrate, the same experiment was repeated but using an inert electrode (glassy carbon (GC) electrode) (Fig. 3). As it can be observed, when an inert substrate is used, the only current density increment is the one due to oxygen and chlorine evolution reactions starting at 1.6 V (Ref 22, 23). Therefore, it can be concluded that the current density increment and the following decrease seen for the bare NiTi alloy are exclusively due to pitting and repassivation of the alloy surface.

To probe into the inhibitory effect of AOT, another experiment was performed. In this case, a potential higher than the one needed to initiate the localized attack of the bare sample was applied (0.65 V). Once again, the tests were executed in Ringer's solution with different AOT concentrations (Fig. 4). It can be seen that the addition of AOT allows obtaining lower current densities compared to the bare sample. The higher the AOT concentration, the lower the current density obtained.

Then, it can be concluded that AOT is an effective inhibitor for the NiTi alloy, given that its presence retards the beginning of pitting and lowers the current density when the sample is already suffering pitting corrosion. Given that AOT is a surfactant, the corrosion protection can be associated with the formation of AOT bilayers/multilayers on the alloy surface for concentrations above the CMC (Ref 16). These self-assembled structures can block physically and/or chemically the surface active sites exposed to Ringer's solution.

Figure 1 Potentiodynamic polarization curves of bare NiTi in Ringer's solution containing different AOT concentrations: (a) 0, (b) 10^{-3} , (c) 10^{-2} and (d) 10^{-1} M. Sweep rate: 1 mV s^{-1} . Initial potential: -0.50 V(SCE)

3.2 Low-Voltage Polarization of NiTi in the Presence of AOT

Taking into account that AOT turned out to be a good corrosion inhibitor for NiTi, it was proposed to polarize the alloy applying a low anodic voltage in the presence of this

Table 1 Pitting potential for bare NiTi alloy in Ringer's solution containing different AOT concentrations

AOT concentration, M	Pitting potential (V versus SCE)
0	0.126
10^{-3}	0.380
10^{-2}	0.656
10^{-1}	0.785

Figure 2 SEM image of a pit formed on the bare NiTi surface after potentiodynamic polarization in Ringer's solution containing 10^{-1} M AOT. The table inset shows the elemental composition (wt.%) obtained by EDX.

Figure 3 Potentiodynamic polarization curves of GC electrode in Ringer's solution containing different AOT concentrations: (a) 0, (b) 10^{-3} , (c) 10^{-2} and (d) 10^{-1} M. Sweep rate: 1 mV s^{-1} . Initial potential: -0.50 V(SCE)

surfactant. A 10^{-1} M concentration was chosen given that the best inhibition results were obtained using this concentration. In addition, it was difficult to prepare a solution with a higher concentration due to the low solubility of AOT. As it was explained in Sect. 2, the pH of the as-prepared solution is 8.4. For comparison purposes, a solution of pH 12 was also used. The alloy was polarized applying 2.0 V during 3600 s using a static electrode and a rotating one ($\omega = 500$ rpm). The curves obtained during the anodic polarization are presented in Fig. 5. As it can be seen, the current densities obtained are between 2 and 3 mA cm^{-2} , which are very low if they are compared to the values obtained for NiTi polarized in solutions containing acetic acid or sodium molybdate (Ref 11, 12).

Potentiostatic anodization of a valve metal such as Ti leads to an immediate current density increase (Ref 10). Due to the rapid thickening of the oxide layer, the current density steeply decays until it reaches a low stationary value. On the contrary, in the case of NiTi, the current density value attained in the first seconds of the experiment was maintained almost constant.

Figure 4 Chronoamperometry of bare NiTi in Ringer's solution containing different AOT concentrations: (a) 0, (b) 10^{-3} , (c) 10^{-2} and (d) 10^{-1} M. Applied potential: 0.65 V(SCE)

Figure 5 Chronoamperometry curves for bare NiTi. A potential of 2.0 V(SCE) was applied in 10^{-1} M AOT solution: (a) pH 8.4, 500 rpm, (b) pH 8.4, without rotation, (c) pH 12, 500 rpm and (d) pH 12, without rotation

This can be interpreted considering that the oxide formation rate is equal to the dissolution rate.

3.3 Corrosion Tests of Anodically Polarized Samples

Several corrosion tests of the anodically polarized NiTi samples were performed in Ringer's solution. In the first place, potentiodynamic polarization curves were recorded (Fig. 6). NiTi_{8.4ω} is the only sample that does not suffer pitting corrosion (Fig. 6, curve b). The rise in current density at 1.4 V is due to oxygen and chlorine evolution reactions (Ref 22, 23). In addition, the formation of bubbles over the electrode was observed during the experiment. The samples NiTi_{8.4} and NiTi_{12ω} do not show an appreciable shift of the pitting corrosion potential, while NiTi₁₂ shows a positive shift of 0.30 V (Fig. 6, curves c, d, and e, respectively).

Tafel plots were also registered for every one of the samples in Ringer's solution. First, they were immersed for one hour until the OCP was stable. Then, the potential was swept at 1 mV s^{-1} from -0.20 to $+0.20$ V versus OCP (Fig. 7). The estimation of corrosion potential, corrosion current density, and anodic and cathodic slopes (E_{corr} , i_{corr} , β_a and β_c) was realized by the Tafel extrapolation method, and the values obtained are presented in Table 2. NiTi_{8.4ω} is the only sample that shows an appreciable positive shift in the value of E_{corr} and lowers the value of i_{corr} in one order of magnitude compared with bare NiTi alloy. The i_{corr} values obtained for the anodized samples are comparable with the values reported for NiTi anodized in different electrolytes (Ref 11, 25). In addition, the protection efficiency (PE) of the different samples was quantified using Eq 1:

$$\text{PE (\%)} = \left(1 - \frac{i_{\text{corr}}}{i}\right) \cdot 100 \quad (\text{Eq 1})$$

where i_{corr} represents the corrosion current densities of the anodized samples and i represents the corrosion current density of the bare NiTi alloy. The obtained results are also presented in Table 2, and it can be observed that NiTi_{8.4ω} provides the higher PE.

In order to test the protection level under more severe conditions, the current density–time response when applying

Figure 6 Potentiodynamic polarization curves registered in Ringer's solution for: (a) bare NiTi, (b) NiTi_{8.4ω}, (c) NiTi_{8.4}, (d) NiTi_{12ω}, and (e) NiTi₁₂. Sweep rate: 1 mV s^{-1} . Initial potential: -0.50 V(SCE)

0.65 V in Ringer's solution was registered for bare NiTi and the anodically polarized samples (Fig. 8). The response of NiTi_{8,4ω} is a stable current density with a low value, in the order of 10^{-5} mA cm⁻², throughout the whole experiment, which lasted 12 hours (Fig. 8, curve a). For the rest of the samples, there was a point where the current density started to rise denoting the breakdown of the oxide film. Nevertheless, it should be noticed that the values of the current densities obtained are much slower than the ones obtained for the bare alloy (Fig. 8, inset). After the polarization applying 0.65 V, the amount of Ni and Ti released in the Ringer's solution was analyzed for NiTi_{8,4ω} and bare NiTi. The results are compared in Table 3, and they confirmed that the oxide film formed during the anodic polarization in the presence of AOT is very protective, given that the concentration of Ti and, more importantly, that of Ni are reduced significantly.

Finally, the OCP was measured for one week for NiTi_{8,4ω} and bare NiTi in Ringer's solution (Fig. 9). The OCP value of NiTi_{8,4ω} is stable during the whole experiment, with a value 0.20 V more positive than the bare alloy, which could be an indicative of an anodic protection mechanism. This was confirmed with the analysis of the amount of Ni and Ti released into the solution (Table 4). Once again, this result confirmed that the oxide layer potentiostatically formed on NiTi in the presence of AOT is very protective given that the released amount of Ti and Ni is almost suppressed.

Figure 7 Tafel plots registered in Ringer's solution for: (a) bare NiTi, (b) NiTi_{8,4ω}, (c) NiTi_{8,4}, (d) NiTi_{12ω}, and (e) NiTi₁₂. Sweep rate: 1 mV s⁻¹

3.4 Anodically Polarized Samples Characterization

Considering all the corrosion tests results obtained for the anodically polarized samples, it was decided to characterize only the sample with the best corrosion performance, that is, NiTi_{8,4ω}. First of all, a SEM image (Fig. 10a) and a general EDX spectrum (Fig. 10b) of the modified surface were taken. The SEM image shows a compact surface without signs of cracks even though the polishing lines are still visible. The EDX spectrum shows the Ni and Ti signals, as expected, but there is no S signal which would be associated with the sulfonate group of the AOT molecules. Prior to the test, the samples were covered with carbon to avoid interference while the images are taken; therefore, the C signal is present. The O signal is also present given that an oxide layer was formed. In general, the spectrum is similar to the one obtained for the bare NiTi which is an indicative that the oxide layer potentiostatically formed is very thin (Ref 26).

Another characterization technique used was XPS. The survey spectrum of the anodically polarized sample is shown in Fig. 11. The main signals obtained, which are indicated, are O1s, Ti2p and C1s. The Ni2p signals would have to appear between 851 and 860 eV (Ref 4, 27) but, remarkably, they were not obtained. The C1s peak, which has a binding energy of 284.64 eV, is attributed mainly to carbon from atmospheric contamination (Ref 28) and/or carbon from the XPS instrument

Figure 8 Potentiostatic response obtained at 0.65 V(SCE) in Ringer's solution for: (a) NiTi_{8,4ω}, (b) NiTi_{8,4}, (c) NiTi_{12ω} and (d) NiTi₁₂. The inset shows the response for bare NiTi alloy

Table 2 Corrosion parameters obtained using the Tafel extrapolation method

Sample	E_{corr} (V versus SCE)	i_{corr} mA cm ⁻²	β_a , V dec ⁻¹	$ \beta_c $, V dec ⁻¹	PE, %
Bare NiTi	-0.288 ± 0.031	$4.66 \times 10^{-4} \pm 4.11 \times 10^{-5}$	0.197 ± 0.004	0.045 ± 0.007	...
NiTi _{8,4ω}	-0.169 ± 0.015	$5.16 \times 10^{-5} \pm 2.20 \times 10^{-5}$	0.152 ± 0.006	0.086 ± 0.020	88.93
NiTi _{8,4}	-0.232 ± 0.035	$1.35 \times 10^{-4} \pm 4.50 \times 10^{-5}$	0.116 ± 0.011	0.102 ± 0.003	71.03
NiTi _{12ω}	-0.386 ± 0.018	$4.59 \times 10^{-4} \pm 1.90 \times 10^{-4}$	0.300 ± 0.012	0.122 ± 0.004	1.50
NiTi ₁₂	-0.262 ± 0.003	$1.59 \times 10^{-4} \pm 9.33 \times 10^{-5}$	0.204 ± 0.009	0.154 ± 0.011	65.88

Table 3: Concentration of Ni and Ti released after anodic polarization applying 0.65 V in Ringer's solution

Sample	Applied potential (V versus SCE)	Time, h	Ni concentration, mg L ⁻¹	Ti concentration, mg L ⁻¹
Blank	...	...	< 0.1	< 0.1
Bare NiTi	0.65	1	18.2	0.93
NiTi _{8,4ω}	0.65	12	< 0.1	< 0.1

Figure 9 Time dependence of the OCP in Ringer's solution for: (a) NiTi_{8,4ω} and (b) bare NiTi alloy

itself (Ref 29). The peak corresponding to O1s at 531.84 eV is mostly due to oxygen bound to Ti (Ref 28).

The high-resolution spectrum of the Ti signal is presented in Fig. 12. The binding energies for Ti2p_{1/2} and Ti2p_{3/2} are 458.24 and 464.02 eV, respectively. According to bibliography, for TiO₂ the distance between both peaks should be 5.7 eV (Ref 27), which is in agreement with the obtained results. Many researchers have described the formation of TiO₂ on NiTi alloy after applying an anodic potential in different solutions, and the binding energies for Ti2p_{1/2} and Ti2p_{3/2} are consistent with the ones reported in this work (Ref 4, 11, 26, 30). It should be mentioned that no metallic Ti component was found, which would have to be found around 454 eV (Ref 27, 28).

The fact that the amount of Ni in the outermost layer of the oxide formed is reduced or not present at all has already been reported (Ref 4, 11, 31). If thermodynamic parameters are checked, TiO₂ formation is favored compared to NiO given that their standard free energies of formation ($\Delta G_{\text{formation}}^\circ$) are - 890 and - 212 kJ mol⁻¹, respectively (Ref 32). Michardi et al. explain that the formation of TiO₂ is progressive and that TiO_x ($x < 4$) might be present underneath the TiO₂ layer (Ref 4). It has also been postulated that Ni⁰ interacts with Tiⁿ⁺ ($n < 4$) and diffuses into deeper layers (Ref 33), which could explain the absence of Ni in the outermost surface. As it was stated before, the presence of a high Ni content in the surface of the alloy might cause infections, allergies, etc. Therefore, the fact that no Ni was found in the outermost surface of the sample NiTi_{8,4ω} is a promising result.

The transport of species through the porous layer of adsorbed surfactants is a complex process (Ref 16). The lower

Table 4 Concentration of Ni and Ti released after OCP measurements during 192 h

Sample	Ni concentration, mg L ⁻¹	Ti concentration, mg L ⁻¹
Blank	< 0.1	< 0.1
Bare NiTi	2.34	< 0.1
NiTi _{8,4ω}	< 0.1	< 0.1

Figure 10 (a) SEM image of NiTi_{8,4ω}, (b) EDX spectrum of NiTi_{8,4ω}

current densities registered during anodic polarization in AOT solution compared to those obtained with other electrolytes can be associated with a decrease in the ionic mobility of diffusion species involved in oxide growth. This is probably one of the reasons that led to the formation of a smooth, thin, and homogeneous film.

The roughness of the anodically polarized sample was measured using AFM. The root-mean-squared (RMS) roughness for the bare NiTi alloy was 9.34 nm (Fig. 13a). In the case of NiTi_{8,4ω}, the RMS was 11.20 nm (Fig. 13b), which means that there is no appreciable change with respect to the bare alloy. The AFM image obtained for the treated sample corroborates the presence of a thin film, given that the polishing lines can be recognized. Ohtsu and Hirano have studied the growth of a TiO₂ oxide layer on NiTi as a function

Figure 11 XPS spectrum obtained for NiTi_{8.4O}

Figure 12 High-resolution XPS spectrum of Ti2p_{1/2} and Ti2p_{3/2} obtained for NiTi_{8.4O}

Figure 13 AFM images of (a) bare NiTi alloy and (b) NiTi_{8.4O}

of time (Ref 8). In their work, during the early stages of the oxide growth, the polishing lines can be observed and the thickness of the layer was less than 30 nm.

Finally, the hydrophilicity of the surface was evaluated by measuring the contact angle. The value obtained for bare NiTi was 70° which is in agreement with the reported bibliographic data (Ref 34). The surface of the anodically polarized sample is more hydrophilic than that of the untreated one given that a contact angle of 63° was measured. The contact angle can vary due to topography, surface energy, and chemical composition of the surface of the material (Ref 35). Given that the changes in the roughness measurements between the anodized sample and the bare alloy were not decisive, it cannot be confirmed that the contact angle variation is because of the surface roughness. However, the XPS analysis demonstrated the absence of Ni and the presence of TiO₂ in the outer layer of the anodized sample. It has been reported that a TiO₂ surface is more hydrophilic than that of the bare NiTi alloy (Ref 34, 36, 37). It has also been reported that the decrease in Ni in the surface of oxidized NiTi slightly increases its total surface energy which is translated as a higher wettability of the surface (Ref 38). In addition, the surfaces that show water contact angles between 30 and 90°, such as NiTi_{8.4O}, are called moderately wettable (Ref 39). Several studies have shown that moderately wettable surfaces favor the adhesion and growth of cells (Ref 40, 41), which could be due to the preferential adsorption of cell-adhesive proteins. This is why surface wettability plays an important role in the biocompatibility of the materials: when the hydrophilicity is higher, more favorable is the surface for cell attachment and proliferation (Ref 42).

4. Conclusions

After several tests in Ringer's solution, it was demonstrated that the surfactant AOT is a good corrosion inhibitor for NiTi alloy. Afterward, an anodic polarization, which consisted in applying a very low anodic potential in AOT solutions, has been successfully used to modify the properties of the native oxide film. The corrosion resistance of the alloy was enhanced, obtaining a remarkable performance for the sample polarized under rotation. The amount of Ni and Ti released under OCP condition and at very positive potentials showed that the dissolution of the alloy was significantly reduced after the anodic polarization.

A smooth, thin and compact film without pores or cracks has been achieved using the low-voltage anodic polarization method. This was interpreted as a result of the micellar assembly of the surfactant on the alloy surface that conditioned the oxide formation process. The XPS technique demonstrates that the oxide grown potentiostatically consists of TiO₂ while no Ni was detected. The corrosion behavior of bare NiTi alloy in chloride solution is principally related to a selective dissolution of nickel element present in the native oxide. The fact that the oxide grown in the presence of AOT does not contain Ni in the outermost layer could explain the excellent improvement in the corrosion protection performance. The decrease in the contact angle value demonstrates that the anodically polarized sample is more hydrophilic than the bare alloy.

Electrochemical results and surface analysis indicate that this low-potential polarization method can be easily used for future applications of the NiTi alloy.

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Conflict of interest

The authors declare that they have no conflict of interest.

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