



Corrosion behaviour of Nitinol alloy coated with alkylsilanes and polypyrrole

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ABSTRACT

Nitinol (equiatomic Ni and Ti alloy (NiTi)) substrate was modified using a coating system formed by a self-assembled film of alkylsilane compounds (propyltrichlorosilane ($C_3H_7SiCl_3$) or octadecyltrichlorosilane ($C_{18}H_{37}SiCl_3$)) and polypyrrole (PPy) doped with sodium bis(2-ethylhexyl) sulfosuccinate (Aerosol OT or AOT). The combination of alkylsilanes and the presence of a voluminous molecule like AOT entrapped into the PPy films improve the pitting corrosion resistance of the substrate in chloride solution. The best performance was achieved with the longest alkylsilane chains, where the PPy film remains adhered to the underlying coating after a pitting corrosion test.

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1. Introduction

Nitinol (equiatomic Ni and Ti alloy (NiTi)) is commonly used as a biomaterial due to its corrosion resistance in corrosive environments and biocompatibility with the human body. The spontaneous formation of a thin passive Ti dioxide film (TiO_2) confers these properties upon the NiTi alloy [1]. Moreover, TiO_2 dominates the surface because it has the most negative standard free energy of formation (ΔG) compared to Ni oxides. Accordingly, for NiO, TiO and TiO_2 , $\Delta G(298\text{ K})$ is -212 ; -495 and -890 kJ mol^{-1} , respectively [2]. However, the oxides formed on the NiTi surface always contain a certain amount of Ni and present a lower self-healing capacity after scratch tests [3]. The main problem related to the use of the NiTi alloy in medical applications such as orthodontics, cardiovascular, orthopaedics, and urology [4,5] is the release of Ni^{2+} and Ti^{2+} toxic ions inside the human body [6–8]. The NiTi alloy is also susceptible to pitting corrosion under anodic polarisation at potentials higher than 0.30 V(SCE) [7]. Therefore, it becomes of special interest to protect the NiTi surface with a biocompatible organic coating like conducting polymers (CPs).

Polypyrrole (PPy) acts as a very good corrosion inhibitor for metal substrates [9] and it is generally regarded as a biocompatible material [10–13]. Nevertheless, adhesion of CPs to a metallic substrate is usually poor but this limitation can be overcome using an adhesion promoter. Options for these promoters are different alkylsilanes, which can be linked with the metal oxide and act as an intermediary to attach other kinds of organic layers, such as PPy [14,15].

In our laboratory, a PPy film was successfully formed on NiTi alloy using a neutral solution of sodium bis(2-ethylhexyl) sulfosuccinate (Aerosol OT or AOT) containing the monomer (pyrrole (Py)) [16]. 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 NiTi alloy covered with the PPy film was subjected to an anodic polarisation in a monomer-free solution. This adhesion improvement was explained considering the formation of a composite material of PPy/oxide and overoxidation of the PPy film. The coating is able to retard the corrosion of the substrate under open circuit potential (OCP) conditions in the chloride solution due to the low mobility of the AOT molecule in the polymer matrix and the formation of the oxide film through interaction between the PPy and the underlying alloy. In addition, the PPy film presented the ability to protect NiTi alloy against localised corrosion [16].

This work focuses on the grafting of alkylsilanes on to NiTi alloy and the subsequent electropolymerisation of the PPy film in order to improve both the adhesion of the polymer and the corrosion resistance properties of the coating system. The expected improvement of the corrosion resistance of NiTi alloy due to this organic coating system makes it a promising alternative as anticorrosive treatment in different biomedical applications.

2. Experimental

Electrodes were prepared with Nitinol SE-508 (Ni: 55.8 wt.%, O: 0.05 wt.%, C: 0.02 wt.%, Ti: balance) rod samples (NDC, Fremont, CA). The rods were embedded in a Teflon holder with an exposed area of 0.096 cm^2 . Before each experiment, the exposed surface area was

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mechanically abraded to a 1200 grit finish using grit silicon carbide papers, then with 3 μm diamond paste and finally washed with triply distilled water. This pretreatment was employed in order to partially remove the natural oxide film formed on the NiTi surface. Finally, the electrode was cleaned by two sonication steps (15 min each) in fresh methanol before immersion in silane solution.

The synthesis of two alkylsilanes (short (C3) and long chain (C18)) films was performed on bare NiTi alloy by simple immersion during 18 h in 1 mM solution of alkylsilanes in hexane (Sigma-Aldrich) with a water content of 0.001%. The hydrolysis and condensation reaction of alkylsilanes were catalysed by a trace amount of water in hexane and the moisture in the air. Two types of alkylsilane compounds (pure Aldrich liquid products) were used:

$\text{C}_3\text{H}_7\text{SiCl}_3$	propyltrichlorosilane	C3
$\text{C}_{18}\text{H}_{37}\text{SiCl}_3$	octadecyltrichlorosilane	C18

Chart 1: alkylsilanes reagents studied.

The samples were then cleaned to remove the physisorbed silanes by sonication in three consecutive steps (15 min each) in fresh hexane first and then in fresh methanol. They were dried in a nitrogen flow and stored under nitrogen atmosphere before characterisation. Following this pretreatment, the electrodes were immediately transferred to the electrochemical cell.

The counter electrode was a large Pt sheet and a saturated calomel electrode (SCE) was used as a reference electrode. All the potential of this work are quoted vs. SCE. A Metrohm cell of 20 cm^3 was employed for the electrochemical studies.

The PPy films were synthesised electrochemically on bare and on self-assembled film covered NiTi alloy using a 0.05 M AOT solution of pH 7 that also contains 0.25 M Py. The corrosion performance of three different systems was analysed in this work: bare NiTi alloy (NiTi), NiTi alloy coated with PPy film (NiTi/PPy) and NiTi alloy covered by both self-assembled films of alkylsilane (NiTi/C3 or NiTi/C18) and PPy film (NiTi/C3/PPy or NiTi/C18/PPy). The experiences were performed in a sodium chloride solution (0.15 M NaCl), an electrolyte which is frequently used to simulate the biological environment. The cell containing AOT solution with monomer was purified under a saturated atmosphere of nitrogen gas at 25 $^\circ\text{C}$.

Electrochemical measurements were made using a potentiostat-galvanostat PAR Model 273A. Each experiment was repeated three times to ensure reproducibility with variations below $\pm 5\%$.

A dual stage ISI DS 130 scanning electron microscope (SEM) (JEOL 35 CF, Japan) operated at 15 kV and an EDAX 9600 quantitative energy dispersive X-ray (EDX) analyser were used to examine the surface characteristics of the electrodes, metalised with gold.

Contact angle (CA) measurement of unmodified and modified NiTi alloy with the self-assembled film of silane was also performed in order to characterise the hydrophobic or hydrophilic nature of the surface. CA measurements were performed at 25 $^\circ\text{C}$ using a 1 μL droplet of triply distilled water and an optical contact angle (OCA 20) system (DataPhysics Instruments GmbH, Germany). CA values reported in this work are the average of three measurements taken after 30 s of stabilisation on the substrate surface.

Adhesion of the PPy film synthesised on NiTi alloy was tested using Scotch® Magic™ Tape 810 (3 M). The 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 peeled 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 with 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. Synthesis of self-assembled film of alkylsilanes on NiTi alloy

The film of alkylsilanes was used in order to modify the surface characteristics of NiTi alloy and to improve the adhesion of the PPy film. The organic coating systems are expected to function as a barrier to prevent the permeation of corrosion accelerants like Cl^- and therefore enhancing the corrosion resistance of the substrate surface. It is known that alkyltrichlorosilanes present a faster hydrolysis–condensation reaction in comparison to the other silanes [17]. However, alkyltrichlorosilanes are not the common choice to modify a metal substrate since these kinds of molecules release the corrosive Cl^- ion after hydrolysis reaction. Contrasted with this traditional belief, our study described below, will reveal some corrosion protection effects of the alkylsilane with long chain ($\text{C}_{18}\text{H}_{37}\text{SiCl}_3$) in concordance with the results previously reported by Huo et al. [18].

The scratches produced to NiTi alloy during mechanical abrading are observed in Fig. 1a. The water CA measured for abraded NiTi alloy was

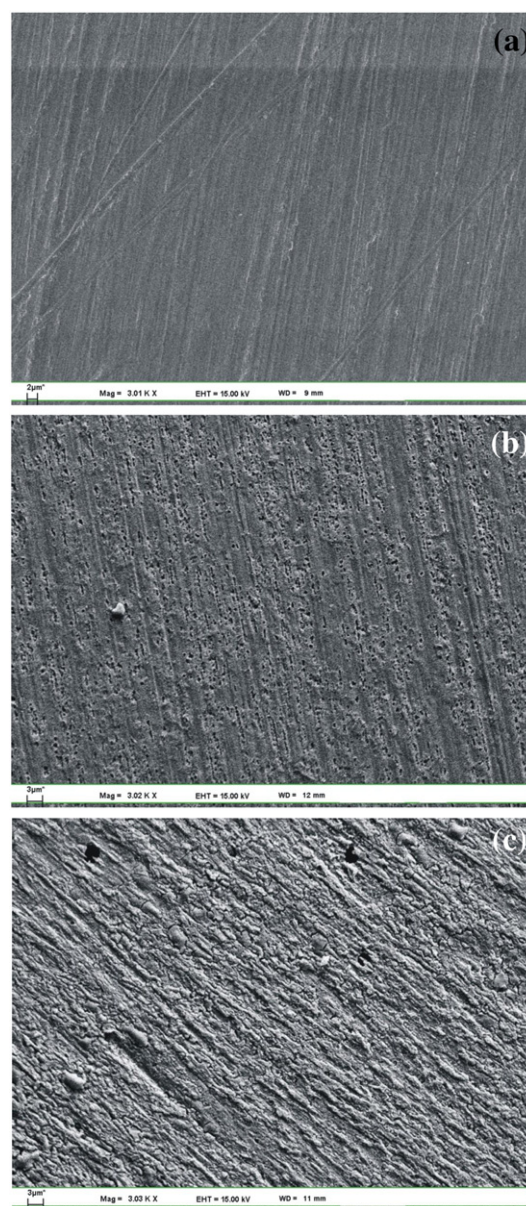


Fig. 1. SEM micrograph of: (a) NiTi, (b) NiTi/C3 and (c) NiTi/C18. The self-assembled films were obtained after immersion during 18 h in 1 mM solution of alkylsilanes in hexane.

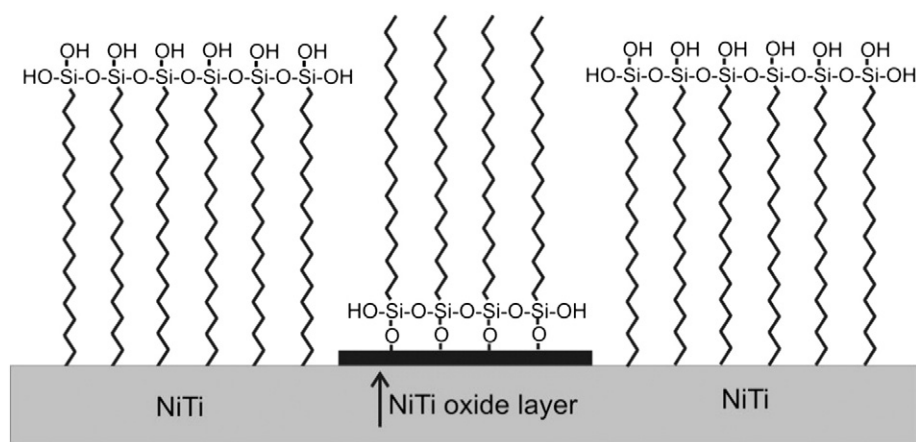


Fig. 2. Schematic representation of initial mixed self-assembled monolayer of $C_{18}H_{37}SiCl_3$ formed on the partially removed oxide layer present on the NiTi surface.

$78 \pm 1^\circ$. There is a concordance between this value and the values recently reported by Shabalovskaya et al. [19] and Tang et al. [20], who had found water CA values of 79.5° and 76.7° , respectively, for mechanically polished NiTi alloy. However, the water CA measured for NiTi alloy covered by a native oxide film was $59 \pm 1^\circ$, which denotes the hydrophilic nature of the passive film. Petrovic et al. [21] have previously reported a water CA value of 63.9° . The increase of water CA value after mechanical abrasion of NiTi alloy indicates a more hydrophobic surface as a result of partial removal of the hydrophilic native oxide film.

It is known that the structure and properties of self-assembled films depend on the chain length of the alkylsilanes [17]. The sample modified with short alkylsilane chain (C3) exhibited very small black dots or pits (micrometre scale), as shown in Fig. 1.b. The release of a large amount of corrosive Cl^- ions after hydrolysis reaction produces the appearance of local corroded areas. However, local corrosion events (pits) were not observed on the sample modified with long alkylsilane chain (C18), according to the SEM image observed in Fig. 1.c. It is possible

that both alkylsilanes (short (C3) and long chain (C18)) formed films on the NiTi surface with the alkyl chains attached to the oxide-free substrate surface generated by mechanical abrading. In both cases the polar $-Si-OH$ bonds, formed by hydrolysis reaction of $-Si-Cl$ bonds, are oriented away from the surface giving place to a hydrophilic surface. The densely packed thin film structure observed in Fig. 1c should hinder the interaction between the Cl^- ions and the inner substrate surface.

The water contact angle values of NiTi/C3 and NiTi/C18 were 41° and 73° , respectively indicating that the NiTi/C3 surface is more hydrophilic than the NiTi/C18 surface. The formation of a mixed self assembled structure (Fig. 2) on top of the partially oxidised alloy surface generated after mechanical abrasion can be proposed. Both molecular orientations ($-Si-OH$ bonds oriented away from the surface and $-Si-OH$ bonds anchored to the oxide) can be formed on the NiTi surface. The contact angle values obtained for water would suggest the idea that a more hydrophilic surface is generated with the short alkylsilane compared with the long one, because in this case the oxide-free area is larger. The

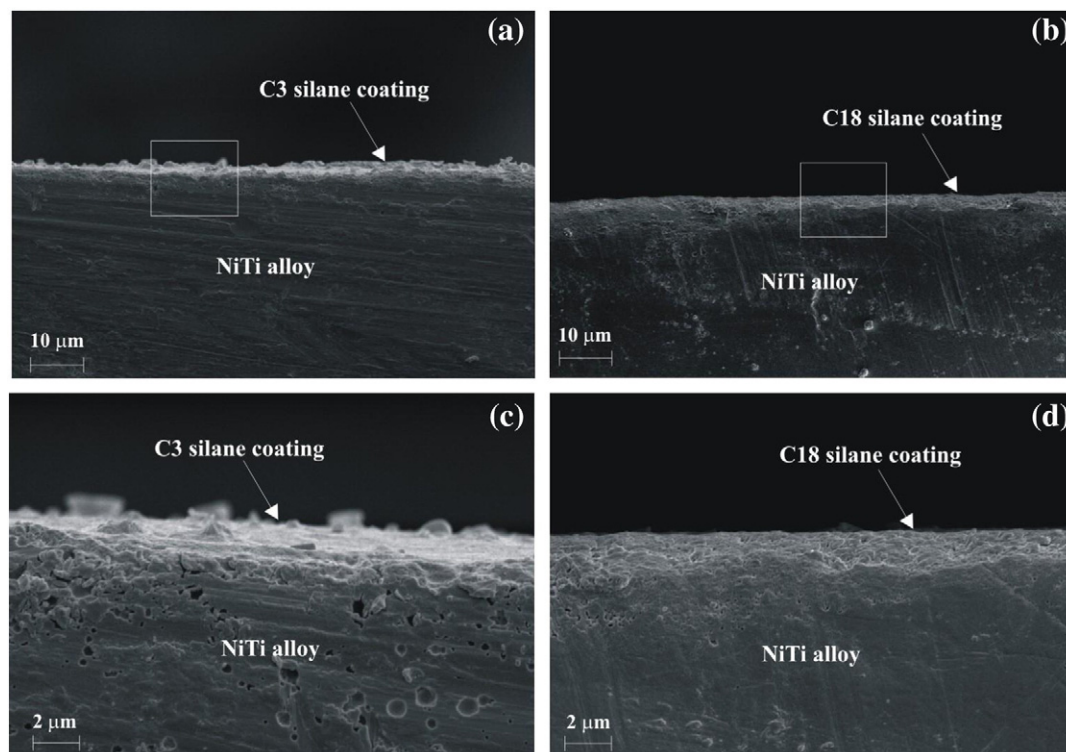


Fig. 3. Cross-section SEM images of NiTi alloy modified with C3 (a) and C18 (b) alkylsilanes. (c) and (d) are amplified images of the marked zones in (a) and (b), respectively.

possible formation of mixed multilayer of long trichlorosilane chain on aluminium 2024-T3 alloy partially covered by Al_2O_3 was proposed by Huo et al. [18].

The cross-section morphology of modified NiTi alloy with short and long alkylsilane chain is presented in Fig. 3. In both cases, well adherent and closed-packed multilayers are observed. The estimated thickness for the C3 and C18 films are 0.9 (Fig. 3c) and 1.3 μm (Fig. 3d), respectively.

EDX analysis performed on the NiTi surface treated with each alkylsilane (C3 and C18) reveals the presence of Si (Fig. 4a and b), indicating that the substrate is covered by the silane. However, the smaller intensity of Ti and Ni peaks observed for NiTi/C18 (Fig. 4b) compared to NiTi/C3 (Fig. 4a), could be related to the more homogeneous and compact film observed in Fig. 1c.

3.2. Electrochemical synthesis of PPy on unmodified and modified NiTi alloy with self-assembled film of alkylsilane

The electrochemical synthesis of PPy film on unmodified and modified NiTi alloy with a self-assembled film of alkylsilane was carried out in 0.05 M AOT aqueous solution of pH 7 containing 0.25 M Py. Polymer growth can be realised by potentiodynamic, galvanostatic and potentiostatic polarisations techniques (Figs. 5–7).

The first cycle for unmodified NiTi alloy in the AOT solution containing the monomer (Fig. 5a) presents an increase in the anodic current density at about 0.50 V(SCE), which corresponds to Py oxidation. A

current loop associated with the nucleation and growth of the polymer is observed in the following negative scan [22]. New oxidation–reduction waves appear whose charges increase with each subsequent sweeping indicating the build-up of polymeric products.

Similar cyclic voltammograms for modified NiTi alloy with films of different alkylsilanes (Fig. 5b and c) were obtained, although the charges associated with the oxidation and reduction of the polymer are lower than those corresponding to unmodified NiTi alloy. This result was explained considering that the presence of hydrocarbon chains reduces the area available for electron transfer reaction and also limits the transport of pyrrole monomers to the alloy substrate. A uniform and homogeneous PPy film was obtained in all cases after potentiodynamic polarisation, although the coating could be completely removed from the surface with a Scotch tape.

The galvanostatic formation of PPy on unmodified and modified NiTi alloy with self-assembled films of alkylsilane is shown in Fig. 6. It was found that the minimum applied current density necessary to produce the electropolymerisation on the NiTi surface previously modified with the silane film was 15 mA cm^{-2} . The response to this current density step shows that the potential decreases until it reaches a constant value of about 0.90 V(SCE). The polymerisation potential of Py for modified NiTi alloy with alkylsilane is higher than that of unmodified NiTi alloy due to the barrier effect of the film (Fig. 6, curve b and c respect to curve a). The typical cauliflower structure of the PPy film was observed in all cases, although the coating could be easily peeled off the surface.

The chronoamperometric curves for PPy electropolymerisation are presented in Fig. 7. It can be observed that for unmodified NiTi alloy the current density increases after an induction time of 1 s leading to the nucleation and growth of the PPy film (Fig. 7, curve a). The oxidation of the NiTi alloy occurs during the first seconds of polarisation in AOT solution without the presence of the monomer (small insert in Fig. 7) [16]. The induction time is not observed in the case of modified NiTi alloy with the film of alkylsilanes (Fig. 7, curve b and c). On the other hand, the current density reached in the case of the NiTi alloy modified with the alkylsilane is lower than the unmodified substrate due to the resistance of the film formed on NiTi alloy. With reference to adhesion, it was found that the PPy film potentiostatically formed was extremely adherent only when the NiTi alloy was modified with long alkylsilane chain. In the last case, the coating could only be removed by mechanical abrasion.

SEM images of the PPy film potentiostatically formed at 0.9 V(SCE) during 600 s on modified NiTi alloy with short and long alkylsilane chain are observed in Figs. 8 and 9, respectively. Fig. 8a indicates that the PPy film is not adhered to the modified NiTi alloy with short alkylsilane chain. The thickness of the PPy film was estimated to be about 25 μm (Fig. 8b). The uncovered PPy region (Fig. 8a, point 2) exhibits very small pits (Fig. 8c), as was previously shown in Fig. 1.b for the modified NiTi alloy with C3 silane thin film. A magnified SEM image of the polymer film (Fig. 8a, point 3) presents the typical cauliflower structure of PPy (Fig. 8d). In the case of modified NiTi alloy with long alkylsilane chain the PPy film with cauliflower morphology (Fig. 9) remains attached to the substrate. The cross-section views of NiTi/C3/PPy (Fig. 10a) and NiTi/C18/PPy (Fig. 10b) systems confirm that the PPy film remains anchored to the NiTi alloy when it is modified with the long alkylsilane chain.

3.3. Corrosion protection performance of the silane/PPy film

Fig. 11 displays the OCP vs. time plot of bare NiTi alloy and modified NiTi alloy with short and long alkylsilane chain in 0.15 M NaCl solution. The curves corresponding to the same three surfaces but covered with the PPy film are also shown in Fig. 11.

As can be seen, the OCP of the bare NiTi alloy (Fig. 11, curve a) shifts towards more negative potentials in the first seconds of immersion until a constant value of -0.58 V(SCE) was attained. Previous results

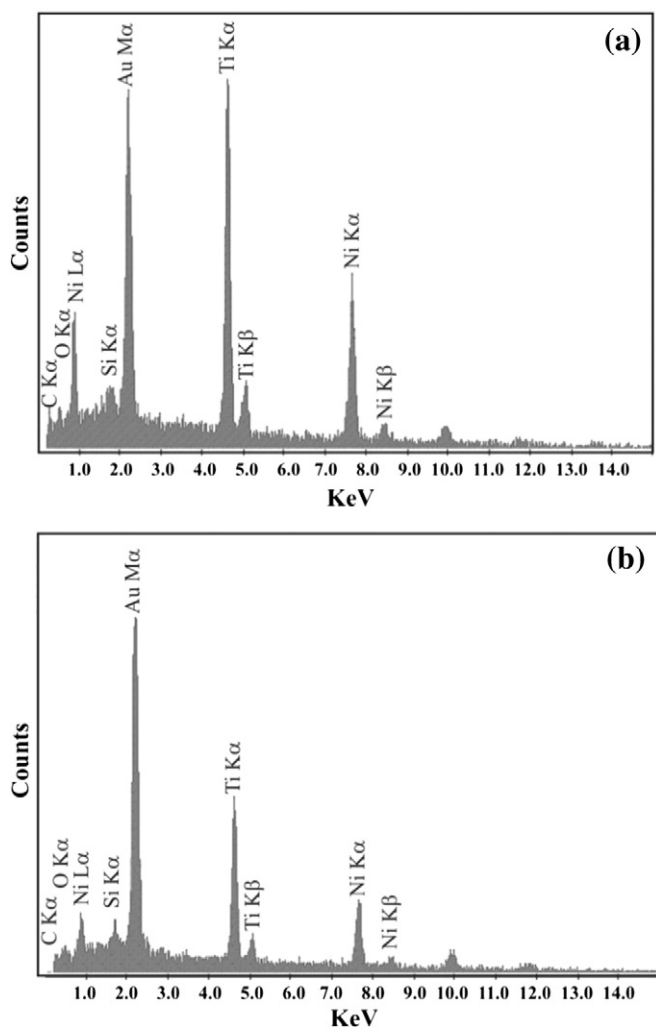


Fig. 4. EDX spectra of: (a) NiTi/C3 and (b) NiTi/C18. The self-assembled films of alkylsilanes were obtained after immersion during 18 h in 1 mM solution of alkylsilanes in hexane.

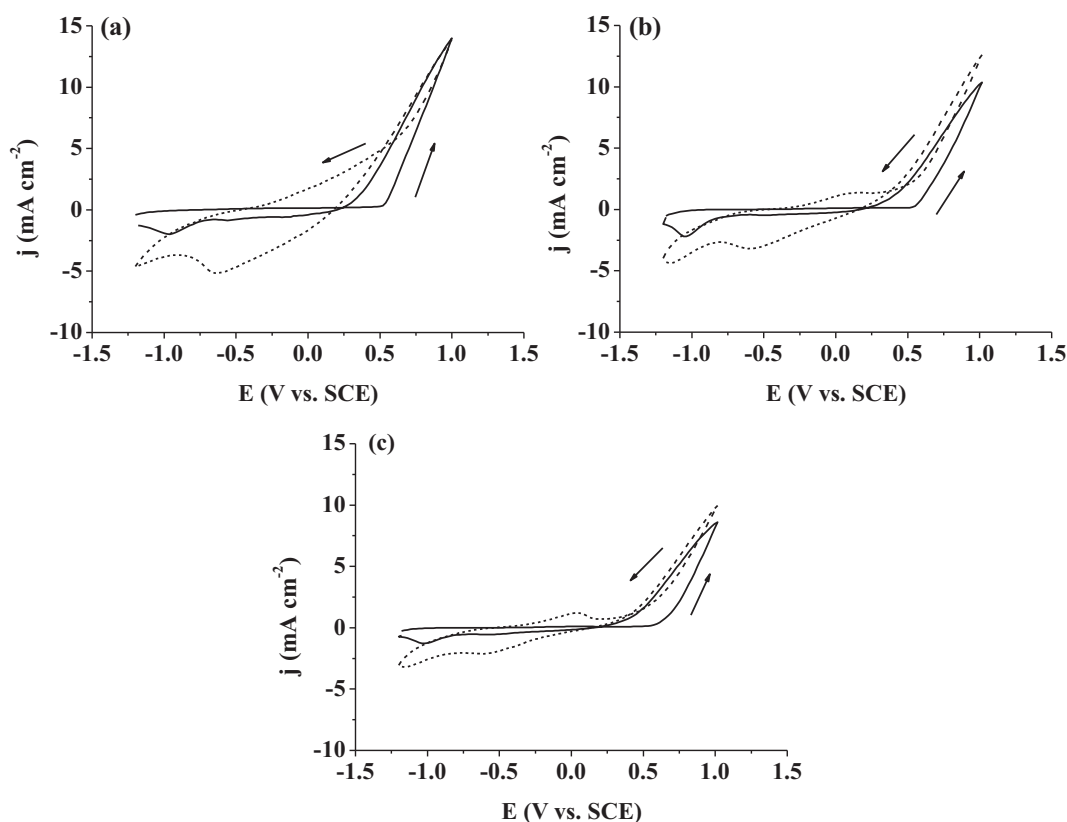


Fig. 5. Cyclic voltammetry obtained in 0.05 M AOT with 0.25 M Py, pH 7 solution for: (a) NiTi, (b) NiTi/C3 and (c) NiTi/C18. The first (full line) and tenth (dotted lined) cycles are displayed. Scan rate: 0.05 V s^{-1} .

indicate that the presence of the oxide film on NiTi alloy confers a more passive OCP value (-0.23 V(SCE)) [9,16]. The OCP value measured indicates that the passive oxide film was undermined after mechanical abrasion.

The OCP values of modified NiTi alloy with short and long alkylsilane chain (Fig. 11, curve b and c) shift slowly in the positive direction reaching a constant value of -0.22 and -0.13 V(SCE) , respectively. Thus, these OCP values for modified NiTi alloy are more positive than that of the unmodified one, indicating the protective actions of the organic film. It has been proposed that this potential represents the equilibrium value of the galvanic coupling of the substrate and the more

noble PPy coating [23,24]. The OCP vs. time plots of all the samples covered with PPy show a similar trend, reaching a constant OCP value within time (Fig. 11, curves d, e and f).

The Tafel curves for the unmodified and modified NiTi alloy in 0.15 M NaCl solution are plotted in Fig. 12. The samples modified with the self-assembled film of alkylsilane present a corrosion current density value two orders of magnitude lower than the unmodified one due to the film, which acts as a physical barrier between the alloy and the aqueous medium (Fig. 12, curve a respect to curve b and c). Moreover,

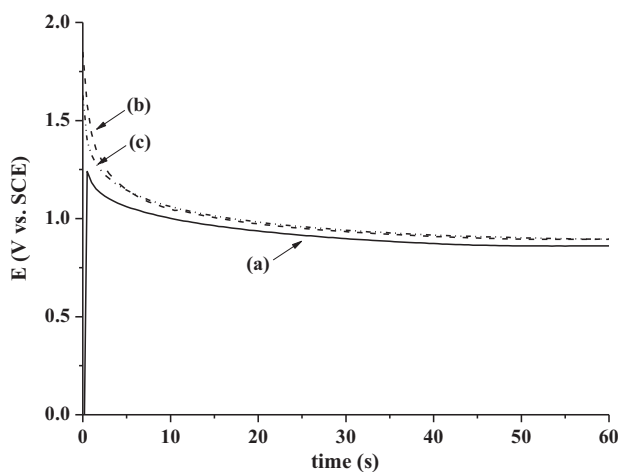


Fig. 6. Galvanostatic response obtained at 15 mA cm^{-2} in 0.05 M AOT with 0.25 M Py, pH 7 solution for: (a) NiTi, (b) NiTi/C3 and (c) NiTi/C18.

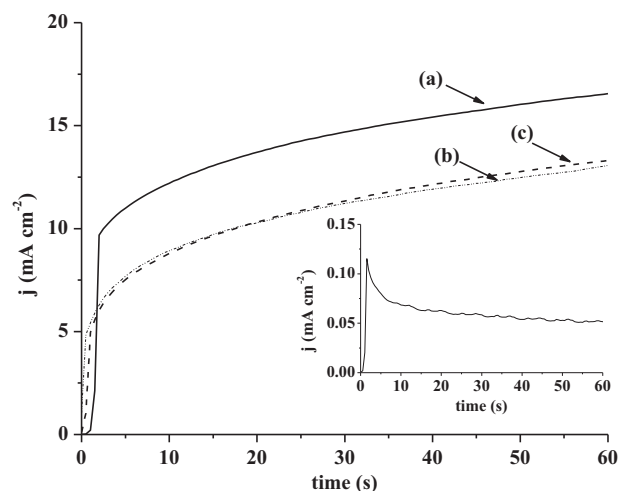


Fig. 7. Potentiostatic response obtained in 0.05 M AOT with 0.25 M Py, pH 7 solution after application of a potential step from 0.0 to 0.9 V for: (a) NiTi, (b) NiTi/C3 and (c) NiTi/C18. Small insert: potentiostatic response to the same potential step obtained for NiTi alloy in 0.05 M AOT, pH 7 solution.

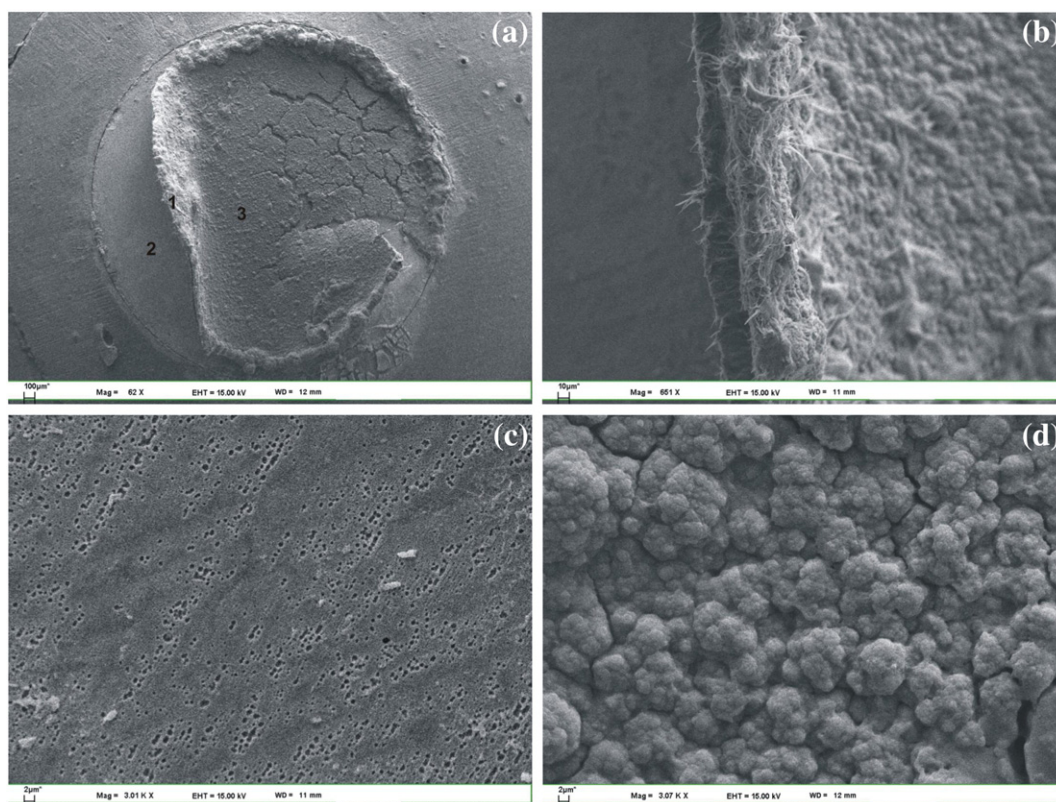


Fig. 8. (a) SEM image of the PPy film potentiostatically formed on the NiTi/C3 system at 0.9 V during 600 s in a 0.05 M AOT with 0.25 M Py, pH 7 solution; (b) magnified image of the detached PPy film (point 1); (c) magnified image of the uncovered PPy zone (point 2) and (d) magnified image of the covered PPy zone (point 3).

the displacement of the corrosion potential to more positive values indicates the protective characteristic of the film in accordance with the results presented in Fig. 11.

The silane/PPy film also produces a positive shift in the corrosion potential, although of a minor magnitude (Fig. 12, curve e and f). On the other hand, the corrosion current densities measured are one order of magnitude smaller than those for the unmodified samples, but they are one order of magnitude bigger than those corresponding to the modified samples with alkylsilane. This result can be interpreted considering that the galvanic interaction between the polymer and the substrate gives rise to oxidation of the substrate and reduction of the polymer.

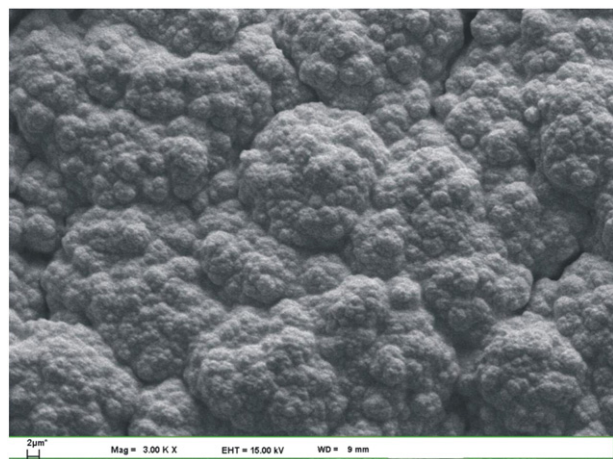


Fig. 9. SEM image of the PPy film potentiostatically formed on the NiTi/C18 system at 0.9 V during 600 s in a 0.05 M AOT with 0.25 M Py, pH 7 solution.

The anodic polarisation curve of bare NiTi alloy in 0.15 M NaCl solution (Fig. 13, curve a) is characterised by a passive region followed by an increase in the current density at approximately 0.05 V(SCE), which indicates the breakdown of passivity. This measured breakdown potential is more negative than the values previously reported [7,16,25], due to the removal of the freshly oxide formed on the surface as a result of the mechanical abrasion. When the bare NiTi alloy is modified with alkylsilanes, the polarisation curves in sodium chloride solution (Fig. 13, curve b and c) indicate an extensive passive region until the current density increases at 1.5 V (SCE) due to the oxidation of water to oxygen over the organic coating. Moreover, the anodic peak observed at -0.25 V(SCE) for the PPy film formed on unmodified and modified NiTi alloy with the self-assembled film of silane (Fig. 13, curve d, e and f) is related to the oxidation of the polymer itself, while overoxidation and oxidation of water occur at more positive potentials.

The current density–time response registered in 0.15 M NaCl solution at a more positive potential (0.65 V vs. SCE) than that corresponding to the breakdown of the bare NiTi alloy is presented in Fig. 14, curve a. After 3600 s of polarisation, the high current density value measured (40 mA cm^{-2}) indicates that localised corrosion of the sample is evolved. As it can be seen in Fig. 14 curve b, the self-assembled film of short alkylsilane does not offer resistance to pitting corrosion of the underlying NiTi. This result can be explained by the pre-existence of black dots or pits formed during the silane hydrolysis reaction. The film of long chain alkylsilane only protected the underlying NiTi alloy during 5400 s, when a sudden increase of anodic current density was observed (Fig. 14, curve c). After that, current spikes were observed indicating that the silane film is no longer protective.

When an unmodified and a modified NiTi alloy with long alkylsilane chain (C18) were covered with PPy film the anodic current density values measured after applying a constant potential value of 0.65 V(SCE) during 15 h in sodium chloride solution were 0.35 and 0.03 mA cm^{-2} , respectively (Fig. 14, curve d and f). These current density values are

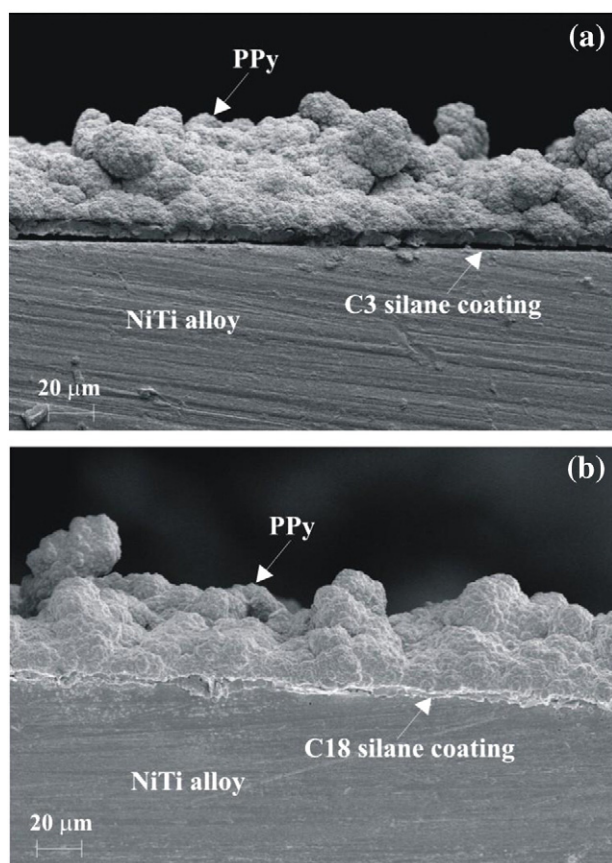


Fig. 10. Cross-section SEM images of NiTi/C3/PPy (a) and NiTi/C18/PPy (b) systems obtained at different magnifications.

significantly lower than that for the bare NiTi alloy. However, when bare NiTi alloy was modified with short alkylsilane chain (C3) and then covered by PPy, the anodic current density remains at a low value during 800 s and then slowly increases until it reaches the value corresponding to the bare NiTi alloy (Fig. 14, curve e). This response can be explained considering the bad adherence between the PPy film and the self-assembled film of short alkylsilane chain (C3). On the contrary, the more compact structure observed for modified NiTi alloy with long alkylsilane chain (C18) in Fig. 1c and the good adherence of the PPy film

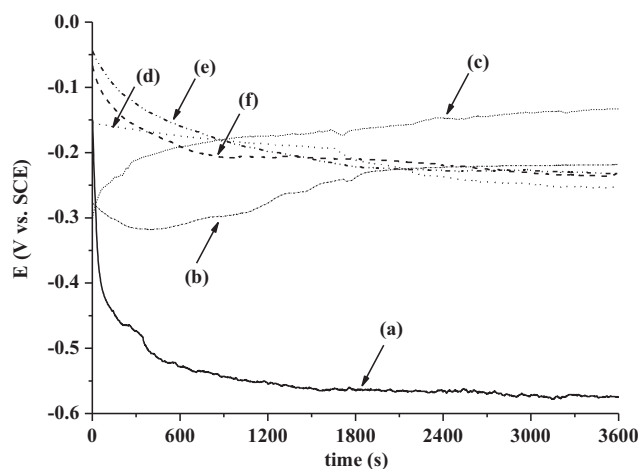


Fig. 11. OCP vs. time plot in 0.15 M NaCl solution for: (a) NiTi, (b) NiTi/C3, (c) NiTi/C18, (d) NiTi/PPy, (e) NiTi/C3/PPy and (f) NiTi/C18/PPy. The polymer was synthesised at 0.9 V during 600 s in 0.05 M AOT with 0.25 M Py, pH 7 solution.

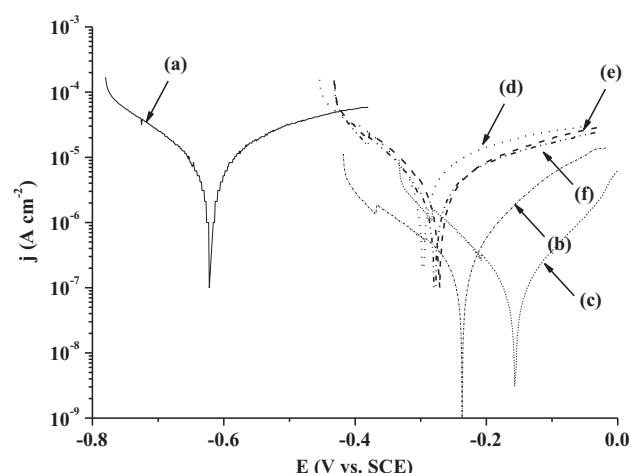


Fig. 12. Tafel curves registered after OCP measurements in 0.15 M NaCl solution at 0.001 V s^{-1} for: (a) NiTi, (b) NiTi/C3, (c) NiTi/C18, (d) NiTi/PPy, (e) NiTi/C3/PPy and (f) NiTi/C18/PPy.

potentiostatically formed confer to the coating system a good performance in pitting corrosion prevention. This result is probably related with the interaction between hydrolysed silanes Si–OH end groups present in the mixed self assembled structure (Fig. 2) and the pyrroles N–H group, as it was previously suggested by Correa et al. [15]. However, the presence of numerous pits on the sample modified with short alkylsilane chain (C3) (Fig. 1.b) results in a bad adherence with the PPy film.

It was found that the PPy film remains adhered to the underlying silane coating after the pitting corrosion test. In addition, the absence of any detectable change in the PPy film formed on modified NiTi alloy with long alkylsilane chain indicates no occurrence of pitting corrosion events even after 15 h of polarisation at 0.65 V(SCE) (Fig. 15).

The redox response of the NiTi electrode covered with the PPy film is similar to that found for the polymer deposited onto Ti [26]. That is, during the switching between the oxidised state and reduced state, a reduction process appears at very negative potentials, which can be attributed to the compensation of the polymer charge by Na^+ insertion [27]. Therefore, the AOT molecule is not easily released from the polymer matrix due to its large size and then cations are the dominant mobile species during switching.

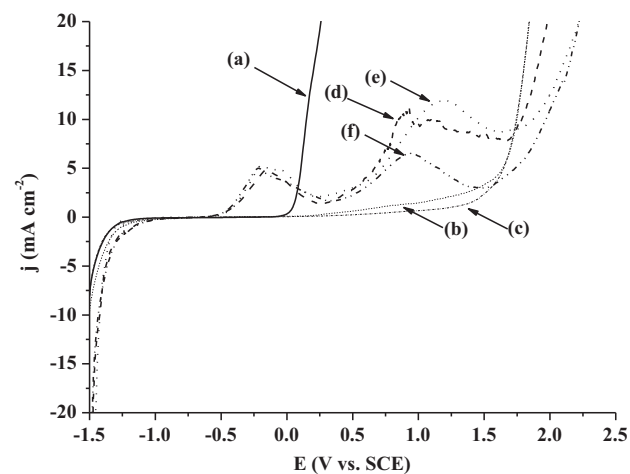


Fig. 13. Polarisation curves registered in 0.15 M NaCl solution at 0.050 V s^{-1} for: (a) NiTi, (b) NiTi/C3, (c) NiTi/C18, (d) NiTi/PPy, (e) NiTi/C3/PPy and (f) NiTi/C18/PPy. The polymer was synthesised at 0.9 V during 600 s in 0.05 M AOT with 0.25 M Py, pH 7 solution.

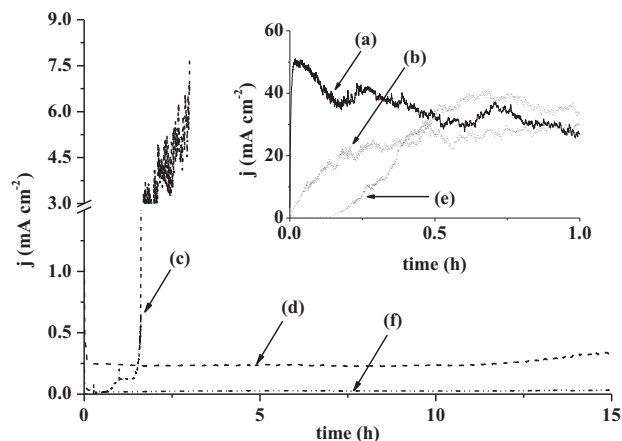


Fig. 14. Potentiostatic response obtained at 0.65 V in 0.15 M NaCl solution for: (a) NiTi, (b) NiTi/C3, (c) NiTi/C18, (d) NiTi/PPy, (e) NiTi/C3/PPy and (f) NiTi/C18/PPy. The polymer was synthesised at 0.9 V during 600 s in 0.05 M AOT with 0.25 M Py, pH 7 solution.

Thus, the improvement in the pitting corrosion resistance of the substrate in chloride solution can be attributed to the following facts: i) the presence of a hydrophobic film of the long alkylsilane; ii) the good adhesion between the silane and the polymer film; iii) the presence of the voluminous AOT molecule entrapped in the polymer matrix, just as it was previously shown [16] and iv) the stabilization of the passive layer as a result of a galvanic coupling between the coating and the substrate.

Different types of surface treatments such as heat treatments, chemical and electrochemical modifications of the NiTi surface, ion implantation, have proved to increase the corrosion resistance of the alloy [28]. Organic [29] and inorganic [30] coatings have also been used to successfully protect NiTi against corrosion. One of the advantages of using conducting polymers is that they have the ability to entrap and controllably release biological molecules. PPy can be modified to make it more suitable for biomedical applications through the incorporation of bioactive molecules [13]. Thus, the present results can serve as a basis for the creation of biocompatible medical coatings.

4. Conclusions

The results reported in this paper show that the chemisorption of long and short chain alkylsilanes on mechanically abraded NiTi alloy produced a mixed self-assembled film. A more homogeneous and compact film was formed with the long alkylsilane. A PPy film was

electrochemically grown on top of the modified electrode. The polymer was adherent only when the electrosynthesis was done under potentiostatic conditions onto the NiTi alloy modified with the long alkylsilane chain.

The best corrosion protection against pitting corrosion was achieved for the NiTi/C18/PPy system owing to the combination of a more hydrophobic nature of alkylsilanes and the presence of AOT entrapped inside the PPy matrix which inhibits the entrance of chloride ions. This outstanding performance is also related with the good adherence between the PPy film and the underlying silane coating.

This kind of organic coating system constitutes a promising alternative as anticorrosive treatment of NiTi alloy for practical applications.

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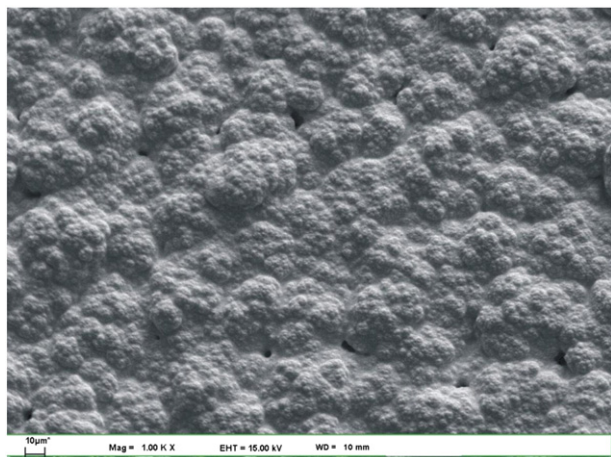


Fig. 15. SEM image of the NiTi/C18/PPy electrode after 15 h of polarisation at 0.65 V in 0.15 M NaCl solution.

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