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Electrodeposition of polypyrrole on Nitinol alloy in the presence of inhibitor ions for corrosion protection

D.O. Flamini *, M. Saugo, S.B. Saidman

Instituto de Ingeniería Electroquímica y Corrosión (INIEC), Departamento de Ingeniería Química, Universidad Nacional del Sur, Av. Alem 1253, 8000 Bahía Blanca, Argentina

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ABSTRACT

The electrosynthesis of polypyrrole (PPy) films on Nitinol (NiTi) from solutions containing different corrosion inhibitors is reported. The corrosion behaviour of the coated samples was investigated in 0.15 M NaCl solution. The presence of molybdate ions in the polymer matrix confers to the substrate a greater resistance to pitting corrosion. The polymer formed potentiostatically in a solution at pH 12 containing nitrate and molybdate is the most efficient in terms of adhesion and corrosion protection. Results are interpreted in terms of the nature of the dopants, the good electroactivity of the polymer and passive properties of the oxide layer.

1. Introduction

Nitinol (an acronym for the Nickel–Titanium Naval Ordnance Laboratory) alloy has been extensively studied as an implant material for biomedical applications (orthodontic wires, self-expanding cardiovascular and urological stents, bone implants and tiny surgery tools) [1,2]. Its good corrosion resistance and biocompatibility with the human body can be attributed to a layer comprised mainly of TiO_2, with a small amount of NiO on the outermost surface layer [3]. Whereas pure titanium shows a wide range of passive state (up to 10 V(SCE)) in physiological solution, NiTi alloy has a smaller range of passivity and is susceptible to localised corrosion (pitting or crevice) at relatively low anodic potentials (between 0.0 and 1.0 V(SCE)) [3–6]. The main issue related to the use of NiTi alloy as a biomaterial is the release of carcinogenic Ni^{2+} and Ti^{2+} ions into the human body [3,7,8]. Finding a solution to this problem has motivated many researchers to study surface modifications and the use of different coatings. Chemical and thermal passivation [3,9,10], laser welding [11], laser melting surface [12], ion implantation [13] and cathodic electrophoretic deposition of functional materials [14] have been used as surface modification treatments to improve the corrosion resistance of NiTi alloy. What is more, different coating treatments for NiTi alloy such as nitride treatment [7], using different silane coupling agents as adhesion promoter of polymer matrix [15], polymerisation of styrene on self assembled monolayer of carboxylic acid [16] and the formation of nanocomposite polymers [17] were also employed to enhance the corrosion performance of NiTi alloy.

It has been demonstrated that PPy is capable of providing corrosion protection. The polymer can be deposited in different ways such as a single film [18,19], as part of a multilayered coating [20,21] or it can be incorporated as an additive in a matrix [22]. PPy is also an attractive organic coating for a large number of biological and biomedical applications due to its biocompatibility with the human body [23]. Moreover, a PPy coating can act as a remarkable corrosion inhibitor for metal substrates although the adhesion of the polymer to the metallic substrate is frequently poor [24]. In a previous paper, we have demonstrated that a PPy film presented the ability to protect NiTi alloy against localised corrosion when it was synthesised in a neutral solution of sodium bis(2-ethylhexyl) sulfosuccinate (AOT) containing the monomer (pyrrole (Py)) [25].

Several corrosion inhibitor ions such as molybdate and citrate have been used to passivate the surface of Ti and Ti6Al4V alloy [26–30]. Furthermore, molybdate ion was used as a corrosion inhibitor of NiTi alloy over a wide range of chloride ion concentrations [31]. In this case, potentiodynamic curves of the NiTi alloy passivated in molybdate solution show a positive displacement of 0.4 V(SCE) in the breakdown potential value when is compared to the non-passivated sample. This result was explained by an increase in TiO_2 content on the outermost surface.

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* Corresponding author. Tel./fax: +54 291 4595182.
E-mail address: dflamini@uns.edu.ar (D.O. Flamini).

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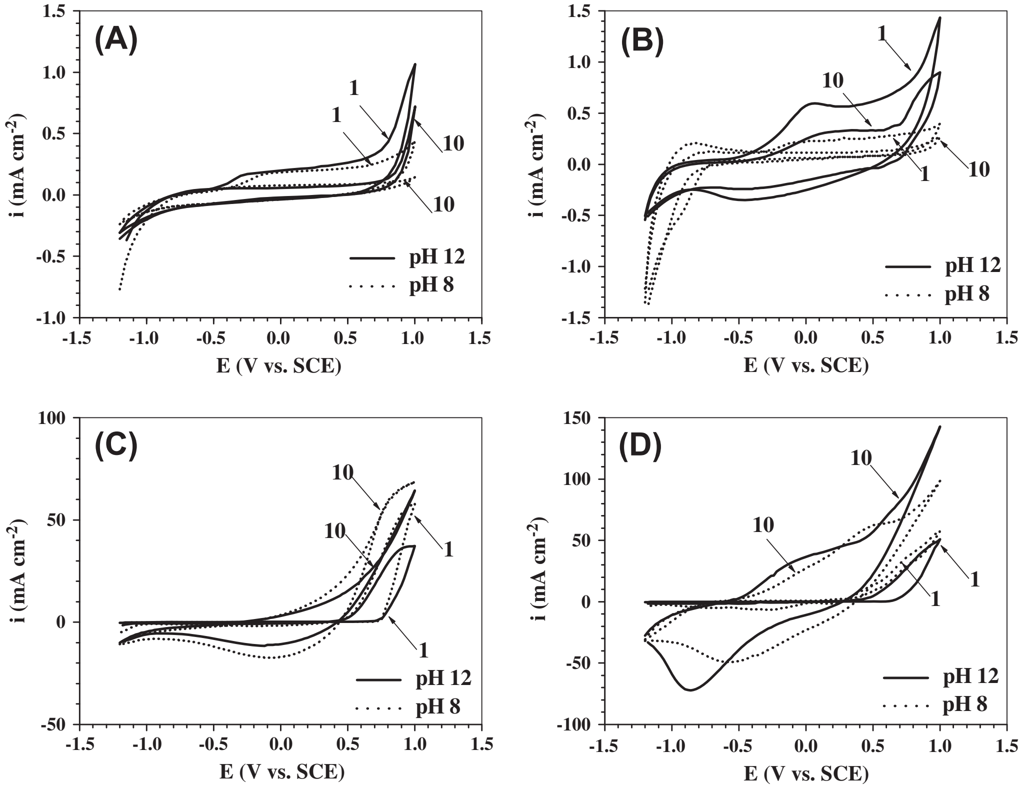

Fig. 1. Cyclic voltammograms obtained for NiTi alloy in 0.35 M NO_3^- solutions at different pH values (8 and 12) containing: (A) 0.12 M $C_3H_5O(COO)_3^{3-}$, (B) 0.12 M MoO_4^{2-}, (C) 0.12 M $C_3H_5O(COO)_3^{3-}$ + 0.50 M Py and (D) 0.12 M MoO_4^{2-} + 0.50 M Py. The first and tenth cycle are displayed. Scan rate: 0.05 V s^{-1}.

The presence of different ions in the electrolyte solution during the electrochemical synthesis of conducting polymers produces coatings with certain characteristics and properties. An improvement of the corrosion protection of 55% Al–Zn-coated steels when molybdate is doped into a PPy layer was found [32]. A recent investigation demonstrated that PPy films electrosynthesised from an alkaline solution of pH 12 containing nitrate and molybdate onto 316L stainless steel have good adhesion and can completely protect the substrate against pitting corrosion in chloride solutions, even when the sample has been polarised at very positive potentials during a considerable period of time [33].

The goal of the present research work was to obtain adherent and protective PPy coatings on NiTi alloy. For this purpose, nearly neutral and alkaline solutions containing different combinations of corrosion inhibitor ions (nitrate and citrate or nitrate and molybdate) were employed during PPy film electrodeposition. To the best of our knowledge, it is the first time that polypyrrole is electrosynthesised on NiTi alloy using inorganic corrosion inhibitor ions. The

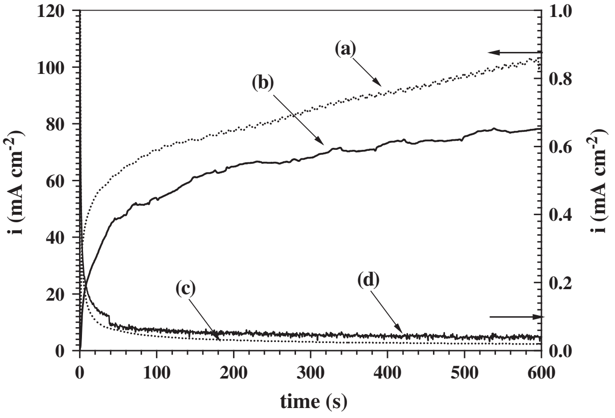

Fig. 2. Chronoamperometric curves obtained for NiTi alloy in 0.35 M NO_3^- + 0.12 M $C_3H_5O(COO)_3^{3-}$ solution containing 0.5 M Py at pH 8 (curve a) and at 12 (curve b), in response to a potential step from 0.0 to 0.80 V(SCE). The chronoamperometric curves obtained in 0.35 M NO_3^- + 0.12 M $C_3H_5O(COO)_3^{3-}$ solution at pH 8 (curve c) and at pH 12 (curve d) without Py, in response to the same potential step are also included.

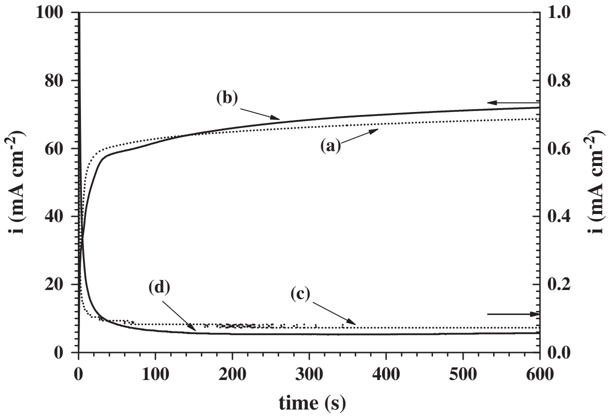

Fig. 3. Chronoamperometric curves obtained for NiTi alloy in 0.35 M NO_3^- + 0.12 M MoO_4^{2-} solution containing 0.5 M Py at pH 8 (curve a) and at 12 (curve b), in response to a potential step from 0.0 to 0.80 V(SCE). The chronoamperometric curves obtained in 0.35 M NO_3^- + 0.12 M MoO_4^{2-} solution at pH 8 (curve c) and at pH 12 (curve d) without Py, in response to the same potential step are also included.