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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.

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, ΔG(298 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:

$C_3H_7SiCl_3$	propyltrichlorosilane	C3
$C_{18}H_{37}SiCl_3$	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 °C.

Electrochemical measurements were made using a potentiostat–galvanostat PAR Model 273A. Each experiment was repeated three times to ensure reproducibility with variations below ±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 °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 ($C_{18}H_{37}SiCl_3$) 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

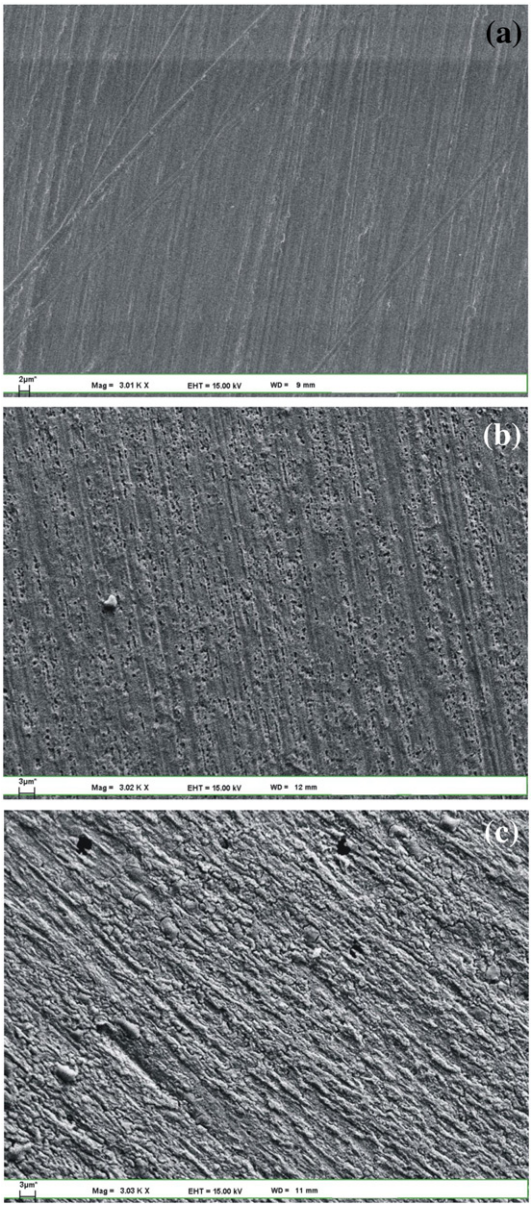

Fig. 1. SEM micrograph of: (a) NiTi, (b) NiTi/C3 and (c) NiTi/C18. The self-assembled films were obtained after immersion during 18 h in 1 mM solution of alkylsilanes in hexane.