Available online at www.sciencedirect.com
SCIENCE DIRECT®

Synthetic Metals 148 (2005) 111–118

SYNTHETIC METALS

www.elsevier.com/locate/synmet

Formation of adherent polypyrrole coatings on Ti and Ti–6Al–4V alloy

Sean T. Earley[a], Denis P. Dowling[b], John P. Lowry[a], Carmel B. Breslin[a,*]

[a] *Department of Chemistry, National University of Ireland Maynooth, Maynooth, Co. Kildare, Ireland*
[b] *Surface Engineering Group, Mechanical Engineering Department, University College Dublin, Belfield, Dublin 4, Ireland*

Received 14 May 2004; received in revised form 19 July 2004; accepted 9 September 2004
Available online 28 October 2004

Abstract

Highly adherent polypyrrole coatings were electrodeposited at etched Ti and Ti–6Al–4V from 0.2 M oxalic acid and 0.2 M pyrrole at a constant applied potential of 0.8 V versus SCE. The substrates were etched in an alkaline peroxide solution at ambient temperature for a 10 min period prior to the electropolymerization reactions. Chemical etching of the substrate gave rise to an increase in the hydrophilicity of the surface, the formation of a micro-etched surface and the formation of a semiconducting titanium oxide film. There was a considerable increase in the density of nucleation sites for polypyrrole growth at the micro-etched surface. Growth of the polypyrrole proceeded slowly from a high number of nucleation sites at the etched surface to give rise to a highly adherent polypyrrole coating. Adhesion of the polypyrrole coating was attributed to micro-etching of the substrate and the conductivity of the oxide film generated during the chemical etching process.

Keywords: Titanium; Polypyrrole; Implant; Adhesion; Electropolymerization

1. Introduction

Over the past number of years there has been various reports in which polypyrrole has been identified as a potential biomaterial, with applications in bioactive coatings for medical implants, microactuators for artificial muscle tissue and time-release membranes [1–3]. Research thus far has been promising with various groups investigating the biocompatibility of polypyrrole [4,5] and its modification in order to produce a novel bioactive product. One of the more interesting applications that have been proposed for polypyrrole coatings is as a bioactive membrane on the surface of prosthetic implants, such as titanium or titanium alloys. In addition, polypyrrole offers the potential to apply a variety of biological modifications, such as the inclusion of hydroxyapatite, doping with species such as biotin and hyaluronic acid, or modifying the surface of the polymer by grafting peptide sequences that can promote a specific cellular response [6–9].

In the case of implant materials, such as titanium or titanium alloys, adhesion of the polypyrrole coating to the implant substrate becomes a very important consideration. Although there are a number of reports in the literature [1,10–17] on the electrosynthesis of polypyrrole, polythiophene and polyaniline at titanium, oxidation of titanium occurs at the potentials required to oxidise the monomers and electrochemically deposit the conducting polymer. This in turn affects the electropolymerization reactions and the generation of adherent conducting polymers at the titanium interface.

In most of the published reports it was found that the nature of the titanium substrate, in particular the titanium oxide, was critical in the deposition of the polymer. For example, De Giglio et al. [1,6] have deposited polypyrrole at titanium from a KCl solution containing 0.4 M pyrrole at a potential of 0.7 V (Ag/AgCl) and have identified the thickness of the native oxide as being critical in forming the polymer. Sin et al. [10] found that a polypyrrole poly(4-styrenesulfonate) composite deposited at titanium could be peeled from the electrode as a free standing film, showing that the adhesive bonding between the titanium oxide and polymer was very

---

[*] Corresponding author. Tel.: +353 1 708 3770; fax: +353 1 708 3815.
E-mail address: cb.breslin@may.ie (C.B. Breslin).

0379-6779/$ – see front matter © 2004 Elsevier B.V. All rights reserved.
doi:10.1016/j.synthmet.2004.09.020

poor, resulting in easy delamination of the coating. Mekhalif et al. [15] found that the presence of an oxide layer on titanium prevented the adherence of polybithiophene films to the substrate. Nevertheless, Rammelt et al. [17] produced adhesive polybithiophene films at titanium dioxide (TiO_2) using a surface-coupling agent, while Idla et al. [2,18] deposited adherent polypyrrole coatings at thin (300–350 nm) layers of titanium deposited at a silicon wafer from sodium dodecylbenzenesulfonate, with prior oxidation of the titanium thin layers by immersion in a boiling solution of ammonia and hydrogen peroxide. Also, adherent polypyrrole coatings have been deposited at titanium from an acidic nitrate solution [14], but these were modified with germanium, while the adherent coatings produced by Wang et al. [12] were deposited from sodium *p*-toluene sulfonate solution, but at a porous titanium dioxide interface. In summary, these reports highlight the difficulty in depositing adherent coatings of conducting polymers at titanium.

In this paper, we present results on the deposition of polypyrrole from an oxalic acid solution at pure titanium and a titanium alloy, Ti–6Al–4V. In order to improve the adhesion of the oxalate doped polypyrrole coatings, an ambient temperature alkaline peroxide etch, described by Lowther et al. [19], was used to pre-treat the polished metal surface. This pre-treatment resulted in superior polypyrrole coatings with excellent adhesion properties and coverage of the metal and alloy surfaces.

2. Materials and methods

Pyrrole (Lancaster) was distilled and stored in the dark at −20 °C prior to use. Oxalic acid di-hydrate (99%, Aldrich) was made to a concentration of 0.2 M in distilled water. The alkaline peroxide etch was composed of sodium hydroxide (BDH, technical grade) and hydrogen peroxide (Aldrich, 30%) diluted in distilled water to the desired concentrations of 0.5 M NaOH and 1.0 M H_2O_2. Hanks balanced salt solution was purchased from Sigma. Electrodes were constructed from chemically pure (99.6%+) titanium and Ti–6Al–4V alloy, obtained from Goodfellow Metals Limited, and encased in a resin/teflon housing to provide a working surface.

Both titanium and the Ti–6Al–4V alloy were polished with 1200 grit silica carbide paper and rinsed well with distilled water before performing the electrodeposition experiment or etching. Etching of the surface consisted of immersion of the electrode in the alkaline peroxide solution at ambient conditions (21 °C) with agitation of the electrode for a 10 min period. The polypyrrole coating was formed potentiostatically from a 0.2 M oxalic acid solution containing 0.2 M pyrrole. The applied potential was 0.8 V (SCE) and the experiment was ceased when the desired charge, or electropolymerization period, was passed. A standard three-electrode cell, with a graphite rod and a saturated calomel electrode was used in all measurements. All electrochemical experiments involving the growth of the polymer were performed with a Solartron 1285 potentiostat.

In the case of the photoelectrochemcial measurements, the electrochemical cell was made of Teflon with a quartz window in the base to allow irradiation of the test electrodes. The illumination source was a 300 W Xenon arc lamp (Oriel Model 6258). The light was passed through a water cooler to remove infrared radiation. The beam was then passed through a series of filters, lenses and mirrors and focused on the stage to illuminate the surface of the exposed electrode. The intensity of the light entering the cell was measured as 250 mW cm^{-2} for unfiltered irradiation (200–900 nm) using a Spectra-Physics CW Laser Power Meter Model 407A. A maximum temperature rise of 1.9 °C was recorded over a 30 min illumination period with this polychromatic illumination procedure.

Electrochemical impedance measurements were performed with a Solartron frequency response analyser (Model SI 1250) in conjunction with an electrochemical interface EI 1286. All impedance data were recorded under open-circuit conditions using a sinusoidal excitation voltage of 10 mV. These data were fit to an appropriate equivalent circuit using a non-linear least squares fitting routine using both the real and imaginary components of the data. Mott-Schottky analyses were performed by measuring the capacitance as a function of potential at 1.0 kHz using an excitation voltage of 10 mV and a sweep rate of 0.01 V s^{-1}.

Images of the surfaces were obtained using an Olympus BX51M metallurgical microscope with a Colourview I digital camera attachment. Contact angle measurements were performed with a Dataphysics Contact Angles System OCA 20 with droplets of deionised water. Profilometry was performed with a WYKO NY1100 Optical Profiling system operated in the vertical scanning interferometry mode. A number of measurements were made across the surface and the results averaged.

3. Results

It was possible to electrosynthesize smooth and uniform coatings of polypyrrole at polished titanium and Ti–6Al–4V alloys from 0.2 M oxalic acid and 0.2 M pyrrole at a constant applied potential of 0.8 V versus SCE. However, the adhesion of these coatings was extremely poor and they were totally delaminated upon performing a simple adhesion test as described by Idla et al. [2]. In an attempt to increase the adhesive properties of the coatings three different surface treatment processes were considered. In the first case, the electrodes were immersed in a boiling solution comprising 25% NH_3, 30% H_2O_2 and distilled water in a 1:1:5 ratio [2]. However, regardless of immersion times (ranging from seconds to minutes) there was no observable increase in the adhesion of the polypyrrole coatings subsequently formed at the modified surfaces from oxalic acid. These results are very different to the findings of Idla et al. [2] who obtained