



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

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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. © 2004 Elsevier B.V. All rights reserved.

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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

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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 photoelectrochemical 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

adherent polypyrrole coatings at a thin layer (300–350 nm) of titanium deposited at a Si-wafer from a dodecylbenzene-sulfonate solution. This may be connected to variations in the nature of the substrate and also the electropolymerization medium. Two other approaches were taken; etching in a 1.0 M sodium hydroxide solution at 50 °C for 30 min and etching in a 0.5 M NaOH/1.0 M H₂O₂ solution at ambient temperature (21 °C) for 10 min [19]. Both procedures were highly successful in enabling the deposition of thin and highly adherent polypyrrole coatings at both Ti and Ti–6Al–4V, but because of the lower temperatures and shorter immersion times, the NaOH/H₂O₂ solution treatment was adopted as the more superior surface treatment.

3.1. Surface pre-treatment of Ti and Ti–6Al–4V

Upon etching the titanium electrode in a 0.5 M NaOH/1.0 M H₂O₂ solution at ambient temperature for 10 min it was observed that the surface of the metal became brown in colour, suggesting a modification of the native oxide layer. Similar observations were made for Ti–6Al–4V, however, the appearance of the brown colour on the surface was not as obvious. In order to explore the significance of this modification, the hydrophilicity, etching characteristics and semiconducting properties of the modified and unmodified surfaces were compared. The results of these experiments are summarised in Table 1 and Figs. 1–3. In Table 1, contact angle measurements are shown for the untreated (polished) and etched Ti and Ti–6Al–4V electrodes. These data reveal that the hydrophilicity of the metal surface increases significantly upon etching. The contact angles measured for the untreated electrodes are characteristic of a significantly hydrophobic surface, but these angles are reduced considerably on etching.

In order to evaluate the etching capacity of the alkaline peroxide solution, the metal surfaces were highly polished with 1.0 μm diamond suspension. The surface roughness of the highly polished sample was then determined using profilometry. The surface was subsequently etched in the alkaline peroxide solution and further analysed in order to compare the polished and etched surfaces. Upon etching, the mirror finish of the surface had dulled considerably and the brown colour of the modified surface oxide was evident. Surface profilometry data for the Ti–6Al–4V indicated that the average surface roughness (R_a) of the 1.0 μm-polished sample was 21.2 nm whereas the average roughness of the surface upon etching was 35.9 nm. Some of the corresponding three-

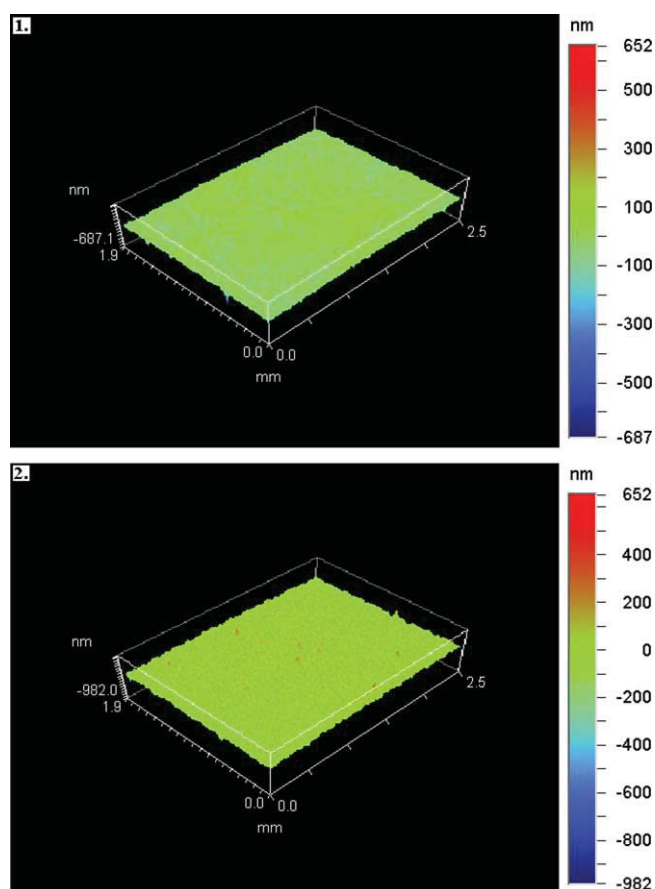


Fig. 1. Plots of the surface profilometry of mechanically polished (1.0 μm diamond suspension) Ti–6Al–4V (1) before and (2) after etching for 10 min at ambient temperature in 0.5 M NaOH and 1.0 M H₂O₂.

dimensional plots are shown in Fig. 1. These results indicate clearly that the alkaline-peroxide etch provides a sub-micron etch of the metal surface.

As the real surface area is clearly modified on etching, Fig. 1, the increase in the area was approximated using double layer capacitance values. The impedance response of both the chemically etched and polished substrates was

Table 1
Contact angle values measured for chemically etched and polished Ti and chemically etched and polished Ti–6Al–4V using deionised water

Metal	Average contact angles (°)	
	Polished samples	Polished and etched samples
Titanium	87.2	40.4
Ti–6Al–4V alloy	80.5	49.2

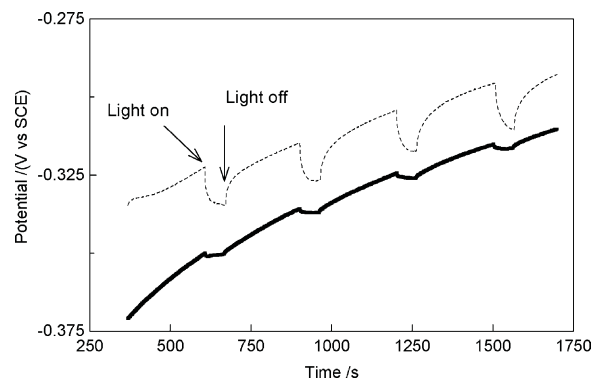


Fig. 2. Open-circuit potential recorded (—) for polished and (---) chemically-etched titanium in Hanks solution with intermittent illumination with polychromatic light.

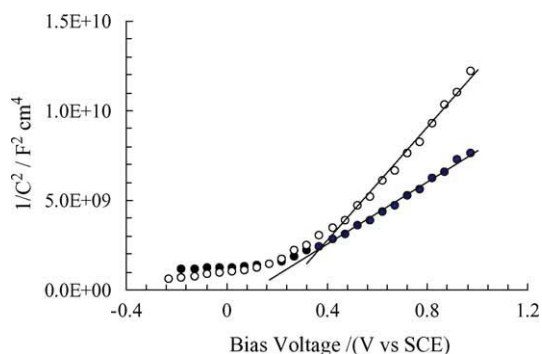


Fig. 3. Mott-Schottky plots recorded in Hanks solution for (●) polished and (○) chemically-etched titanium.

recorded as a function of time under open-circuit conditions in Hanks solution. Using an equivalent circuit, consisting of a solution resistance, the double layer capacitance in parallel with the charge transfer resistance and a diffusion term, the double layer capacitance was calculated as a function of immersion time. The steady-state double layer capacitances (recorded following 12 h of immersion in Hanks solution) of the polished and etched electrodes were measured as 5.2×10^{-5} and 9.5×10^{-6} F cm $^{-2}$ (both normalized to the geometric area), respectively, for the titanium system. This gives a difference of 1.8 in the capacitance. This in turn, corresponds to an increase in the surface area by a factor of 1.8 on chemical etching, which compares well with the data presented in Fig. 1 for the highly polished substrate. A similar approach was used for the Ti-6Al-4V electrode, and a similar increase in the surface area was observed on etching.

The semiconducting properties of the oxide layers formed on the polished and etched electrodes were studied using a combination of photo-potential and Mott-Shottky measurements. In Fig. 2, the open-circuit potentials are shown as a function of time, in Hanks solution, for the etched and untreated Ti electrodes with intermittent illumination of the surfaces. The photoactivity of the etched titanium electrode is seen clearly. Upon illumination of the surface, a sharp drop in the open-circuit potential is seen ($\Delta E = 15$ mV), whereas the open-circuit potential reverts slowly to more positive values on switching off the light. This is consistent with the behaviour of an n-type semiconductor on illumination [20,21]. On comparing the behaviour of the untreated and etched titanium substrates, it is clear that the etching treatment gives rise to the formation of an n-type TiO $_2$ semiconducting oxide phase; oxidation of the untreated electrode only occurs slowly in the Hanks solution. A similar effect was observed with the Ti-6Al-4V electrode. However, the photo-potential was somewhat lower, with ΔE being of the order of 3 mV. This may indicate a lower rate of oxidation of the Ti-6Al-4V electrode during treatment in the alkaline peroxide solution, but it is more likely due to the presence of the alloying components in the oxide film formed on the alloy [22].

Further information on the semiconducting properties of the films formed on the etched and polished surfaces was obtained using Mott-Schottky analyses to estimate the donor density and flat-band potential of the films. These parameters can be estimated using the well-known Mott-Schottky equation.

$$\frac{1}{C_{sc}^2} = \frac{2}{q\epsilon\epsilon_0 N_D} \left(E - E_{fb} - \frac{kT}{q} \right) \quad (1)$$

In this analysis, C_{sc} represents the space charge capacitance, N_D the donor density, E_{fb} the flat-band potential, ϵ the dielectric constant of the semiconductor film (i.e. 120 for the rutile phase and 50 for the anatase phase of TiO $_2$ [23]), ϵ_0 the permittivity of free space, kT is 4.06×10^{-21} J at the measurement temperature, and q is the electronic charge. In the measurements, the potential was swept from the open-circuit potentials adopted by the electrodes in Hanks solution at a sweep rate of 0.01 V s $^{-1}$ in the positive direction and the impedance of the system was measured at 1000 Hz. The data were normalized to the geometric surface area of the polished electrode and then a further correction (of 1.8) was added to accommodate for the increase in the surface area on etching. The total capacitance, C , which consists of contributions from the space-charge capacitance and the Helmholtz capacitance, was calculated from the impedance data. Then, the space-charge capacitance was calculated by correcting this measured capacitance data for Helmholtz contributions using a conservative value of 30 μ F cm $^{-2}$ for the Helmholtz capacitance.

Typical Mott-Shottky plots recorded for the polished and etched titanium electrodes are shown in Fig. 3. The plots exhibit reasonably well-defined linear portions over a relatively wide potential region, and are characteristic of those for an n-type semiconductor, in agreement with other publications [23]. The donor densities, calculated from the slopes of the linear regions of the plot were found to be $1.34 \pm 0.41 \times 10^{18}$ cm $^{-3}$ for the polished titanium electrode and $7.38 \pm 0.43 \times 10^{17}$ cm $^{-3}$ for the electrodes exposed to the etching treatment. The flat-band potentials were calculated as $+0.12 \pm 0.05$ V(SCE) for the polished electrode and -0.08 ± 0.08 V(SCE) for the etched electrode. The calculations were averaged over four determinations. The donor densities calculated here are in reasonably good agreement with those calculated previously for TiO $_2$ [23,24]. Again these data show clearly that the oxide films present on the titanium substrate are different for the polished and etched substrates, with the oxides formed during the etching process having a lower donor density. Similar results were obtained on comparing the donor densities and flat-band potentials of the etched and polished Ti-6Al-4V substrates; for the etched electrode N_D and E_{fb} were $2.18 \pm 0.43 \times 10^{17}$ cm $^{-3}$ and -0.08 ± 0.07 V, respectively, and for the polished electrode N_D and E_{fb} were $2.26 \pm 0.40 \times 10^{18}$ cm $^{-3}$ and 0.13 ± 0.07 V, respectively.

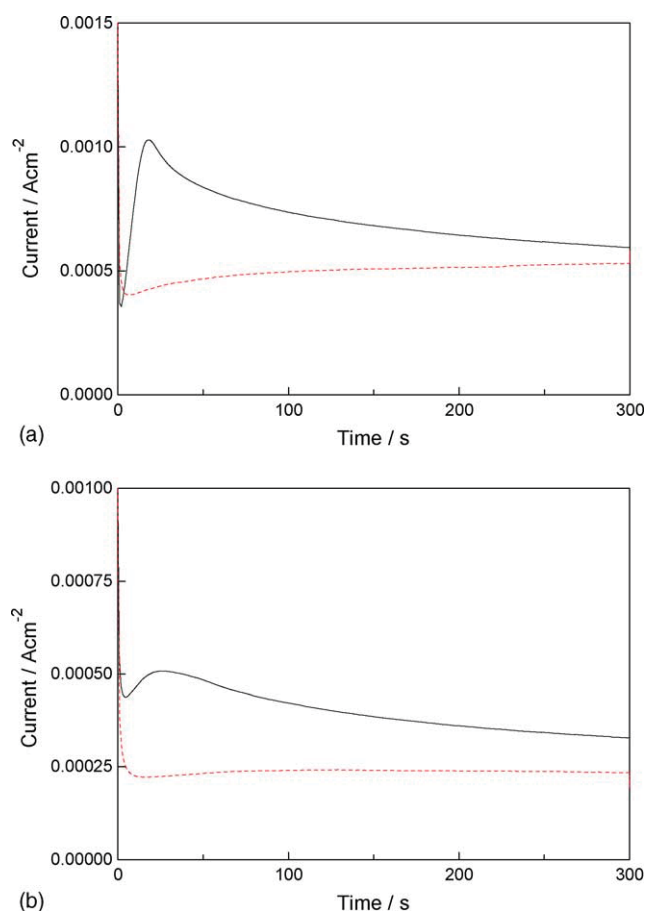


Fig. 4. Current–time transients recorded for deposition of polypyrrole from a 0.2 M oxalic acid solution with 0.2 M pyrrole at 0.8 V vs. SCE at (a) (---) polished and (—) chemically-etched titanium and (b) (---) polished and (—) chemically-etched Ti–6Al–4V.

3.2. Deposition of polypyrrole

Upon deposition of polypyrrole on polished and alkaline-peroxide etched titanium and Ti–6Al–4V a variety of different characteristics were observed, including a change in the current–time transients obtained on potentiostatic deposition of the polymer, a change in the morphological features of the polymer and a considerable difference in the adherence of the polymers to the metallic substrates.

The current–time transients recorded during the electrochemical deposition of polypyrrole at polished and etched titanium and at polished and etched Ti–6Al–4V are shown in Fig. 4(a) and (b), respectively. Again, the current was normalised to take account of the greater surface area of the etched substrate. In the case of polished-only metals a gradual and constant current rise is observed throughout the first 300 s of the experiment, Fig. 4. This is contrasted with the formation of a distinct current peak within the first minute of deposition for the etched surfaces. These observations suggest that a different nucleation process occurs in the initial stages of polymer formation on the electrode surfaces.

In order to gain further insight into this nucleation phenomenon, a light microscope was used to obtain images of the early stages of polypyrrole deposition on pure titanium and Ti–6Al–4V alloy. Typical micrographs recorded for the Ti–6Al–4V surface are shown in Fig. 5 for electropolymerization times of 1.0, 5.0, 10.0, 20.0 and 60.0 s. These images indicate that there is indeed a notable difference in the nucleation properties observed on polished-only and on the etched Ti–6Al–4V surface. The deposition on polished Ti–6Al–4V appears to involve the gradual formation of a number of discrete particles of polypyrrole, which over time increase in size to eventually give coverage of the electrode surface. In the case of polished and chemically etched Ti–6Al–4V, the gradual formation of larger particles, ca. 50 μm in diameter, is evident but more importantly there is an abundance of smaller particles, ca. 5–10 μm in diameter, visible over the entire surface. This is particularly evident following 20 s of electropolymerization. Following these experiments, there was a very significant difference in the adhesion of the polymer films; very poor adhesion was observed for the polished electrode, but excellent adhesion between the etched substrate and polypyrrole was observed.

These observations on the nucleation of the polymer are consistent with the current–time transients shown in Fig. 4. The current peak is seen at about 25–35 s for the etched Ti–6Al–4V electrode. This corresponds to the time period at which the maximum number of nucleation sites are actively involved in promoting polypyrrole growth, Fig. 5. In contrast, the growth of polypyrrole at the polished surface, which involves only a limited number of nucleation sites, proceeds at a near-steady rate, resulting in a near constant current for the duration of polymer growth. This difference in the nucleation of active sites at both the polished and etched surfaces can also be used to explain the considerable difference in the adhesion of the polypyrrole coatings. At the polished electrode, the polymer appears to grow laterally from the original nucleation sites (Fig. 5 at $t = 20$ and 60 s). Bonding between the substrate and the polymer is restricted to the original nucleation sites, leaving relatively large areas of non-bonded polypyrrole. Consequently, it is not surprising that these polymer films have very poor adhesion. In contrast, the much higher density of nucleation sites at the etched surface results in greater adhesion between the substrate and the polypyrrole film.

Upon comparing the micrographs of complete polypyrrole coatings on polished and etched surfaces, morphological differences become apparent. Typical data, showing the morphology of polypyrrole coatings grown for a period of 30 min, are presented in Fig. 6(a) and (b) for the polished and etched Ti–6Al–4V substrates, respectively. The coating on the polished surfaces appears to be thicker than that on the etched surface; more detail of the polishing lines is visible on the surface of the etched metal. However, it should be noted that there was a significant variation in the uniformity of polymer thickness at the polished surface; there were sizeable surface areas with a very thin layer of polymer. Also, it

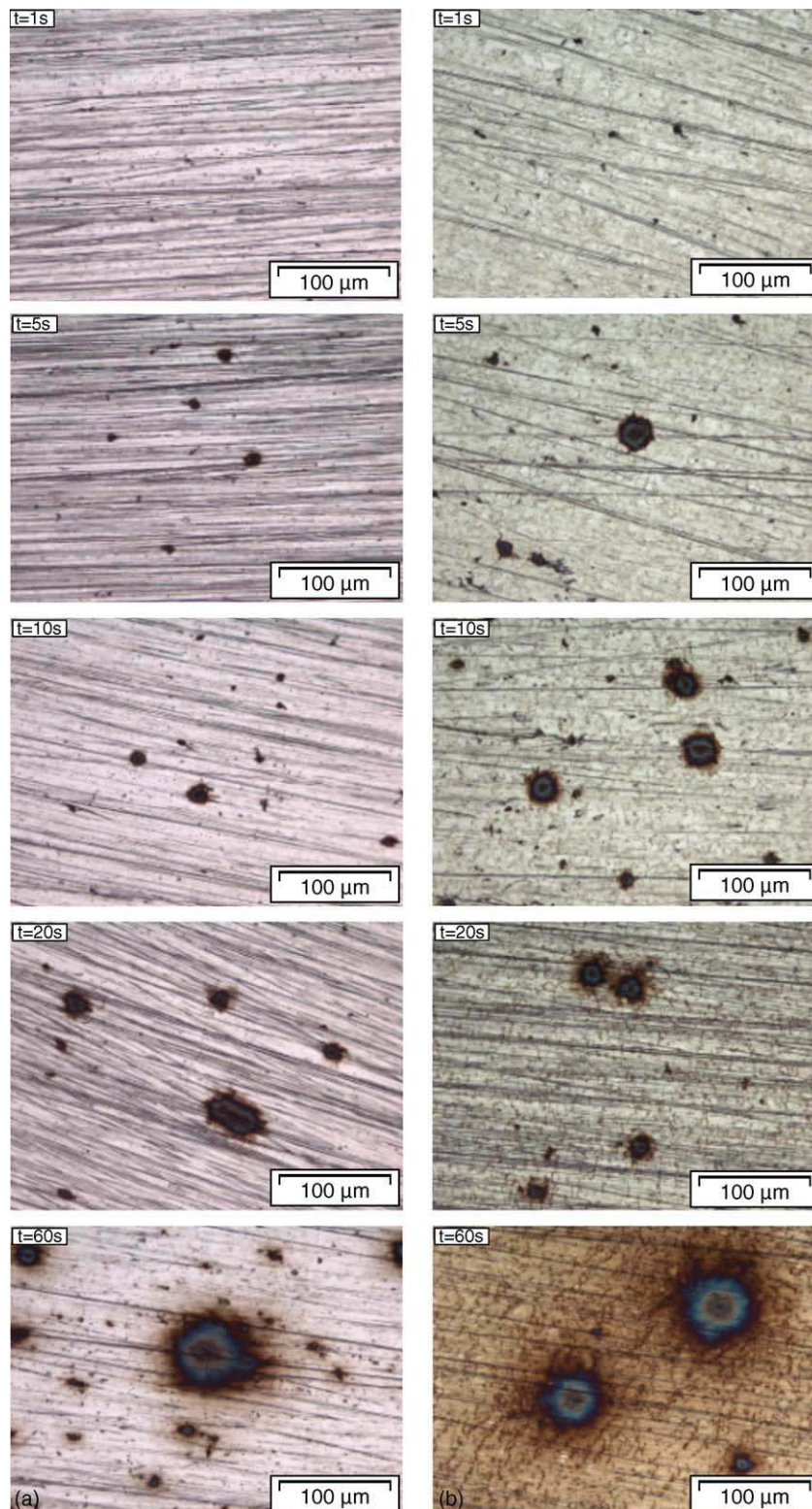


Fig. 5. Surface images obtained during the early stages of polypyrrole deposition from a 0.2 M oxalic acid solution with 0.2 M pyrrole at 0.8 V vs. SCE at 1.0, 5.0, 10.0, 20.0 and 60.0 s for (a) polished Ti-6Al-4V and (b) chemically-etched Ti-6Al-4V.

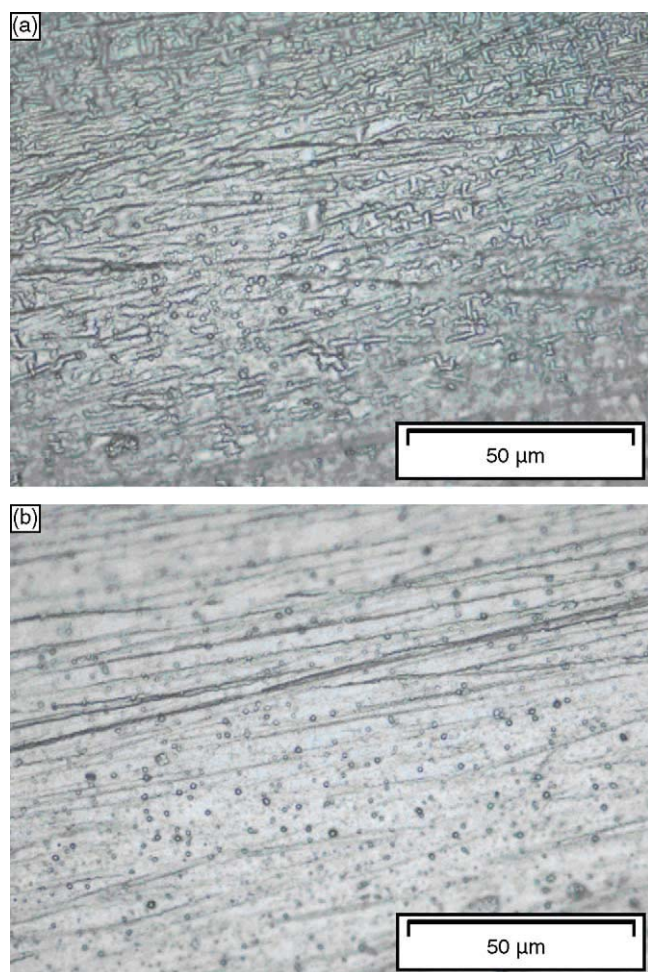


Fig. 6. Surface images recorded following a 30 min electropolymerization period from a 0.2 M oxalic acid solution with 0.2 M pyrrole at 0.8 V vs. SCE for (a) polished Ti-6Al-4V and (b) chemically-etched Ti-6Al-4V.

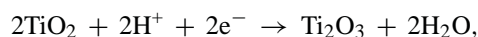
appears that the polymer formed at the etched surface is more compact and smoother.

In an attempt to determine if the considerably enhanced adhesion of polypyrrole at the etched titanium electrode was due to etching of the surface or the nature of the oxide layer generated during the etching process, the oxide layer at the etched surface was further modified. Polypyrrole was then deposited at the modified surfaces and the adhesion of the polymer tested. The first set of experiments consisted of reducing the etched titanium electrode at -1.0 V for 30 min in Hanks solution. Following reduction, the photopotential of the reduced etched surface was measured. There was a considerable reduction in the photopotential from the value of 15 mV recorded for the etched electrode, Fig. 2, to values less than 1 mV for the reduced etched surface. This clearly indicates that the reduced oxide phase contains a very low concentration of Ti(IV), with the reduction step converting the Ti(IV) to the lower oxidation states of Ti(III) or Ti(II). On depositing the polypyrrole at this surface, very good adhesion of the polymer to the surface was obtained indicating

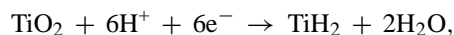
that the oxidation state of titanium in the oxide phase has little influence on the adhesion of the polymer. However, growth of the polymer was inhibited considerably on anodising the titanium substrate in 0.5 M NaOH at 1.0 mA cm^{-2} . This indicates that further growth of the oxide phase gives rise to an interface that is too insulating to enable the electropolymerization reactions.

4. Discussion

It is clear from the results presented that the adhesion of the electrodeposited polypyrrole at bulk titanium and Ti-6Al-4V depends crucially on the nature of the metallic surface prior to the electropolymerization step. This has been highlighted in earlier publications, but there is little data available to enable a determination of the factors that control the formation of adherent polypyrrole deposits at titanium [1,2,18]. It is evident from the presented results that etching of the titanium and Ti-6Al-4V substrates in 0.5 M NaOH/1.0 M H_2O_2 solution at ambient temperature (21°C) for 10 min results in an increase in the hydrophilicity of the surface, Table 1, the formation of a micro-etched surface, Fig. 1, and the formation of an oxide layer with semiconducting properties, Figs. 2 and 3. The observed semiconducting properties of the oxides formed indicate that the oxides contain a sufficiently high concentration of Ti(IV) and accordingly TiO_2 . However, it is well known that oxide films formed at titanium contain Ti(IV), Ti(III) and Ti(II) [24] and consequently the films formed on etching are also likely to contain Ti(II) and Ti(III). However, the actual oxidation state of the titanium in the oxide film seems to have little influence on the adhesion of the polypyrrole. On reduction of the etched titanium substrates in Hanks solution at -1.0 V for 30 min, the Ti(VI) is converted to Ti(III), Eq. (2). Indeed, the formation of TiH_2 is likely, Eq. (3) [24,25].



$$E^\circ = -0.091 \text{ V} \quad (2)$$



$$E^\circ = -0.47 \text{ V} \quad (3)$$

Although these reduced etched surfaces may be oxidised during the electropolymerization reactions at 0.8 V, if the oxidation state of titanium in the film was an important factor then the early polymer nucleation reactions and adhesion of the polymer should be affected. This was not observed.

Adherence of the electrodeposited polypyrrole appears to be connected directly with the manner in which the polymer is nucleated at the titanium and Ti-6Al-4V interface, Figs. 4 and 5. It is very clear from Fig. 5 that growth of the polymer at the untreated electrode involves the establishment of a few nucleation sites. This is followed by uni-directional

growth at the nucleation site without the initiation of any more nucleation sites. Instead, the polymer grows over the native oxide giving very poor adhesion. The significantly higher number of nucleation sites at the etched surface is probably connected with the micro etching and increase in the hydrophilicity of the etched surface. However, the conductivity of the oxide phase is also an important factor. Indeed, on anodising the titanium substrate at current densities of 1.0 mA cm^{-2} , the electropolymerization reaction is almost completely inhibited. The anodised films are too insulating to enable the electron transfer and growth of the polymer. Indeed, the lack of development of new nucleation sites at the polished electrode may be connected with facile oxidation of the air-formed film in the oxalic acid solution at 0.8 V. On the other hand, the semiconducting film generated at the etched surface, although initially less conducting than the thin air formed film, enables polymer growth because the etched surface, with a high concentration of defects or flaws, facilitates the initiation of a high density of nucleation sites. Consequently, after a 30 min electropolymerization period a more compact, highly adherent and thin polypyrrole coating is formed at the etched titanium or etched Ti–6Al–4V substrate, Fig. 6.

Oxidation of the substrates during the early stages of nucleation is likely also to depend on the composition of the electropolymerization solution. The specific role of the electrolyte medium in the nucleation and growth of polypyrrole at titanium is currently under investigation.

5. Conclusions

Adherent polypyrrole coatings were electrodeposited at Ti and Ti–6Al–4V using a two-step process; etching of the substrate in 0.5 M NaOH/1.0 M H_2O_2 solution at 21 °C for 10 min followed by electropolymerization from 0.2 M oxalic acid and 0.2 M pyrrole at a constant applied potential of 0.8 V versus SCE. 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. Adhesion of the polypyrrole coating was attributed to micro-etching of the substrate and the conductivity of the semiconducting oxide film. The etched surface provided a much higher number of nucleation sites for polymer growth resulting in the formation of highly adherent polypyrrole coatings.

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