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Electrochemical preparation of protective oxide coatings on titanium surgical alloys

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This paper reports a novel electrochemical method for the preparation of protective titanium oxide coatings to improve the corrosion resistance and biocompatibility of the Ti6Al4V surgical alloy. Scanning electron microscopy (SEM), electron dispersive spectroscopy (EDS), Auger electron spectroscopy (AES), and the X-ray diffraction technique were used to characterize the structure and the chemical composition of the oxide coatings. *In vitro* electrochemical corrosion studies were also conducted to assess the effectiveness of the oxide coatings in reducing the metal-ion release from Ti6Al4V. The results suggest that the coating process may provide an effective means for improving the corrosion resistance and biocompatibility of titanium surgical alloys under physiological conditions.

1. Introduction

Titanium and its alloys are finding increasing applications in the fabrication of surgical implants such as artificial joints, bone plates, and dental implants. There has been considerable interest, especially in the use of Ti6Al4V alloy, for orthopaedic implants because of its biocompatibility and fatigue strength. However, occasionally, metal-ions have been detected in tissues close to titanium implants [1]. The problem of ion release is particularly of concern in the case of porous-coated orthopaedic implants due to their relatively large surface area. For such implants, the chemical and cellular response of the surrounding tissues to metal-ion release is critical in determining the extent of new bone formation and its subsequent bonding to the implant surface. For example, inhibition of apatite formation by titanium and vanadium ions has been demonstrated [2].

Several surface modification techniques have been proposed to minimize the rate of ion release from titanium surgical alloys. These include chemical passivation [3], ion implantation [4], and anodization techniques [5]. A limitation common to all these methods is that the protective layers formed (normally less than 2 μm) are not sufficiently thick. As a result, the implant may lose its surface protective layer in the long term, particularly when it is submitted to fretting. Thick coatings of titanium oxide, however, can be applied to surgical implants by plasma spray techniques at high temperatures [6], but there are major problems associated with this method. The plasma spray deposition technique is a line-of-sight process which produces a non-uniform coating when applied to porous and non-regular substrates. Non-uniform coatings create local exposure of the metal implant and may provoke a local increase in metal-ion release. Because of the high temperature involved, this technique has also the potential of altering the fatigue properties of titanium implants.

This paper reports a novel electrochemical method for obtaining uniform and relatively thick (up to 40 μm) titanium oxide coatings at ambient temperatures. The method involves direct synthesis of titanium methoxide ($Ti(OCH_3)_4$) by anodic oxidation of titanium in methanolic electrolytes and its rapid hydrolysis and conversion into titanium oxide in the presence of water.

2. Materials and methods

The electrolyte used in this work for the preparation of the oxide coatings was made by adding 10 g of analytical reagent sodium nitrate ($NaNO_3$) to 1 l of analytical reagent methanol containing less than 1% water. Rectangular samples of Ti6Al4V surgical alloy (5×1 cm^2) were mechanically polished and used as the substrate (anode). In certain experiments, the samples were blasted with steel grits (average diameter approximately 0.5 mm) to produce rough substrates. The cathode of the electrolytic cell was also made of a commercial titanium alloy having a surface area of 10×1 cm^2. A Hokuto Denko (HD) HAB-151 potentiostat/galvanostat operating in galvanostatic mode was used to maintain constant current densities during the process.

Thick oxide coatings were obtained using current densities ranging from 5 to 20 mA cm^{-2}. The thickness of the oxide layer, which is governed by the quantity of the current and duration of the process, was varied from 1 to 40 μm. Scanning electron microscopy (SEM), electron dispersive spectroscopy (EDS), Auger electron spectroscopy (AES), and X-ray diffraction analysis were used to characterize the oxide coatings. Electrochemical corrosion studies were also

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conducted to evaluate the effectiveness of the coatings in reducing the metal-ion release from Ti6Al4V.

3. Results and discussion

3.1. Structural and chemical characterization of the oxide coatings

3.1.1. Scanning electron microscopic examination and EDS analysis

Fig. 1 shows the SEM micrograph of the cross-section of a typical oxide coating prepared on a mechanically polished Ti6Al4V substrate at a current density of 7 mA cm^{-2} and 25 °C for 1 h. An interesting feature of the coating obtained on polished substrates is that the outer surface of the coating is extremely smooth regardless of its final thickness. The coating prepared on polished and roughened substrates was found to be dense, uniform, and adherent. Fig. 2 shows the electron dispersive spectra (EDS) of the oxide coating. Besides titanium and oxygen, aluminium, carbon, and nitrogen were also detected in the whole depth of the coating. In contrast, no vanadium was detected in the coating.

3.1.2. Auger electron spectroscopic analysis

The depth elemental analysis was also conducted by using Auger electron spectroscopy (AES) in combination with ion sputtering and mechanical thinning of the coating. 2 keV Xe ions were used for sputtering, with a sputtering rate of approximately 10 nm min^{-1}, as calibrated for Ta_2O_5. The coatings were examined at three areas: (a) close to the surface; (b) close to the centre; and (c) close to the interface between the coating and the titanium substrate (Fig. 3). The dominance of the Ti and O signals in AES spectra indicates that the coating mainly consists of a titanium oxide. The shape and position of the Al peaks also correspond to an oxidized form of aluminium. Carbon and nitrogen were also found in the whole depth of the coating but no vanadium was detected, in agreement with the EDS results. Vanadium, however, could be detected in Ti6Al4V alloy only after complete removal of the oxide coating. It seems, therefore, that the coating process may provide an effective means for excluding vanadium from the surface of Ti6Al4V and thus improving the biocompatibility of this alloy.

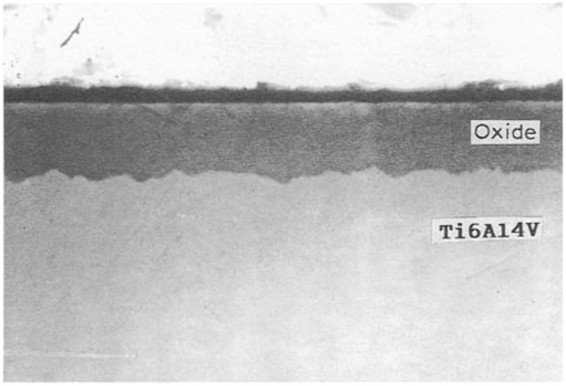

Figure 1 SEM micrograph of a typical titanium oxide coating prepared on a polished Ti6Al4V substrate at 7 mA cm^{-2} for 1 h at 25 °C (×800).

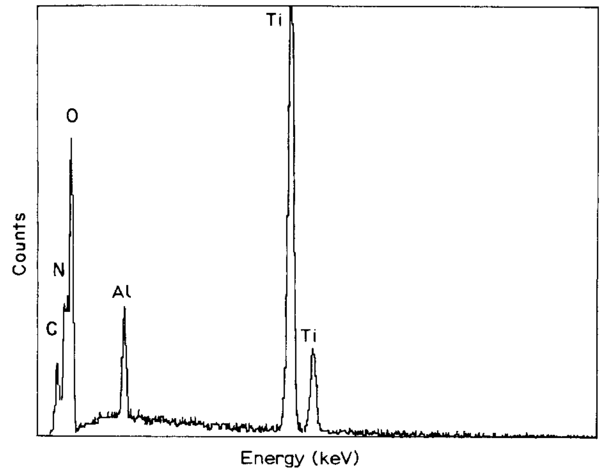

Figure 2 EDS spectra of the titanium oxide coating (spot analysis close to the centre in the coating), as prepared at 7 mA cm^{-2} for 1 h at 25 °C.

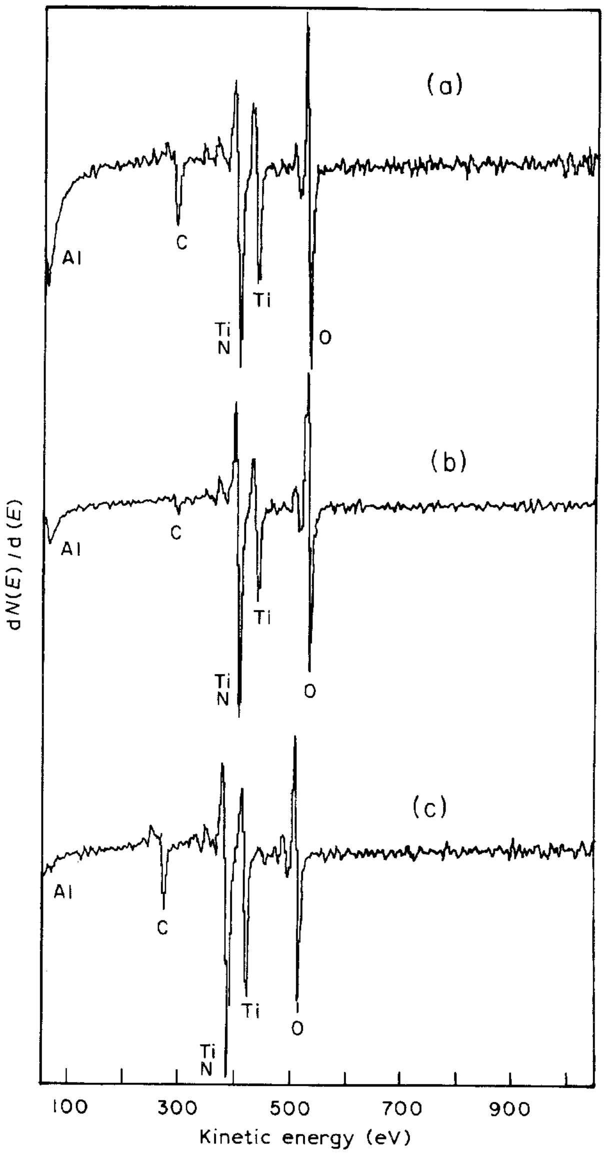

Figure 3 AES spectra (a) close to the outer surface of the coating, (b) close to the centre, and (c) close to the interface of the oxide and substrate.

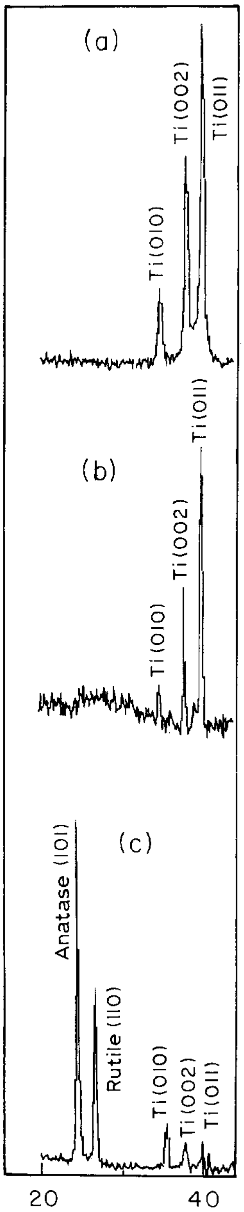

Figure 4 X-ray diffraction pattern of (a) untreated Ti6Al4V substrate, (b) oxide-coated Ti6Al4V, as prepared at 25 °C, and (c) oxide-coated Ti6Al4V, after thermal treatment at 800 °C in air for 1 h.

3.1.3. *X-ray diffraction analysis*

The X-ray patterns of the oxide coatings, as prepared at room temperature and after thermal treatment at 800 °C in air for 1 h, are presented in Fig. 4. The X-ray diffraction of the oxide coating, as prepared, is almost identical to the X-ray pattern of the Ti6Al4V substrate. This indicates that the coating, as prepared at room temperature, may only consist of amorphous phases of titanium oxides. X-ray diffraction analysis of the thermally treated coating, however, revealed that the amorphous coating could be converted into a crystalline form of titanium oxide consisting of rutile and anatase.

3.2. Electrochemical evaluation of the coatings

In vitro electrochemical corrosion studies were also conducted to evaluate the effectiveness of the oxide coatings in reducing the metal-ion release from the Ti6Al4V substrate. These tests consisted of the generation of anodic polarization curves, using a potentiodynamic technique at a sweep rate of 10 mV min^{-1}. Ringer's solution ($T = 37$ °C, pH $= 7$) containing dissolved O_2, N_2, and CO_2 was used as the corrosion cell electrolyte. This solution simulates the majority of inorganic chemical species of human extra cellular fluid. Fig. 5 shows the potentiodynamic polarization curves for untreated Ti6Al4V and for the coated samples, as prepared at room temperature and after thermal treatment in air at 800 °C. Passive behaviour was exhibited by all samples over the entire experimental range of potential. However, coated samples exhibited significantly lower passive currents. The rest potentials (E_r) of the coated samples before and after thermal treatment were also noticeably more noble than that of the untreated Ti6Al4V alloy substrate. These results clearly indicate that the oxide coating may act as an effective barrier in reducing the corrosion rate of titanium implants under physiological conditions. The improved protection offered by the thermally treated coatings may be attributed to the presence of the rutile phase in these coatings, which is the most stable form of titanium oxide.

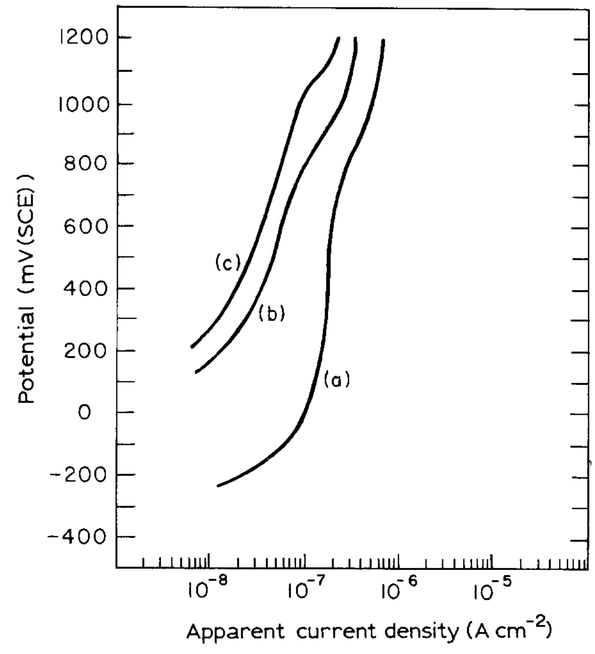

Figure 5 Anodic polarization in Ringer's solution: (a) untreated Ti6Al4V substrate ($E_r = -280$ mV), (b) coated Ti6Al4V as prepared at 25 °C ($E_r = +80$ mV), and (c) coated Ti6Al4V after thermal treatment at 800 °C in air for 1 h ($E_r = +200$ mV).

4. Conclusions

In conclusion, experimental results suggest that the coating process offers a promising means for improving corrosion resistance and biocompatibility of titanium surgical alloys. An attractive feature of the process is that it allows uniform and thick oxide coatings to be applied to porous and non-regular implants. Another characteristic feature of the process is that it also permits the formation of thick and smooth oxide coatings on polished substrates. Such smooth coatings may, indeed, be of interest for a number of biomedical applications. For example, thick and biocompatible coatings with a mirror finish are required to minimize bioadhesion and prevent thrombus formation on the implants that come in direct contact with blood. Other uses of these coatings may be for applications where the friction should be minimized.

Acknowledgements

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