Electrochemical behaviour of TiO_2 nanotube on titanium in artificial saliva containing bovine serum albumin

C. L. Liu[1,2], Y. J. Wang[2], M. Wang[1], W. J. Huang[1] and P. K. Chu*[3]

Titanium that has been anodised to develop a nanotubular titanium oxide film is gaining interest as a dental implant material. In the present work, the corrosion behaviour of the nanotubular titanium has been investigated and compared with that of the mechanical polished titanium in artificial saliva containing bovine serum albumin (BSA, 5 g L^{-1}). The results indicate that the diameter of TiO_2 nanotube plays an important role in controlling the potentiodynamic polarisation behaviour, and the existence of TiO_2 nanotube enhances the corrosion resistance and reduces the corrosion current density, which is more beneficial to the adsorption of BSA compared with the mechanical polished titanium, leading to a notable increase in the corrosion resistance of the outer TiO_2 nanotubular layer.

Keywords: Biomaterials, TiO_2 nanotube, Corrosion, Bovine serum albumin, Artificial saliva

Introduction

Titanium and its alloys, used as dental implants, show good corrosion resistance because of the existence of oxide layer. However, it is hard for the surface to directly bond to living bone after implantation into the host tooth, which influences the initial implant stability due to the poor osseointegration, therefore, surface modification of titanium implants has been used to enhance osseointegration.[1–3] Recently, a self-organised nanotubular TiO_2 layer formed on titanium by anodisation in a fluoride solution made of NaF, NH_4F, or HF has gained great interest, which benefits cell adhesion and deposition of bone-like components.[4,5] As dental implants, the implant bone interface and the gingival implant interface can be formed. The maintenance of the latter is very important.[2] Because the nanoporous titanium has high surface area, beneficial to the in-leakage of aggressive ions; however, the corrosion of nanoporous titanium dental implants may ensue in the oral environment after implantation.[6] Once corrosion occurs, the integrity and structure of the TiO_2 nanotubes may be destroyed gradually.

A few researchers have studied the electrochemical stability of TiO_2 nanotubes. Jang *et al.*[6] and Saji and Choe[7] found that the corrosion resistance decreased for TiO_2 nanotubes on the surface of Ti–Nb and Ti–13Ni–13Zr alloys.[6,7] In contrast, Demetrescu *et al.*[2] and Yu *et al.*[8] reported that TiO_2 nanotubes increased the stability of titanium surface. Considering that the corrosion behaviour of biomedical metals is governed by the interaction between the materials surface and electrolyte, the electrolytes without organic components were involved in the aforecited studies. Furthermore, the influence of serum proteins on the corrosion behaviour of titanium has been found, which was attributed to the adsorption or chelation effect of proteins.[1,9] Several earlier studies have indicated that the adsorption behaviour of protein was controlled by the nanometric microstructure,[10] which might cause the variation of corrosion behaviour of the nanotubular titanium in simulated body fluid containing proteins. It is pity that the effect of proteins on their corrosion behaviour has not been shown up to now.

The major objective of this study was to investigate the corrosion behaviour of the nanotubular titanium in artificial saliva containing bovine serum albumin (BSA) and to compare its corrosion behaviour with that of the mechanically polished Ti control (designated as MPT) by electrochemical tests.

Material and methods

Sample preparation and characterisation

After polishing and ultrasonic cleaning, titanium foils (2 mm thick and 99·5% pure) were anodised for 30 min in 0·5 wt-% hydrofluoric acid using a DC power supply with a graphite electrode as the cathode. Three different voltages of 10, 15 and 20 V were used to produce four different types of nanotexture designated as NT05, NT15 and NT20 respectively. Immediately after anodisation, the samples were rinsed in deionised water before further experiments. The surface topography of the

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[1]School of Materials Science and Engineering, Chongqing University of Technology, Chongqing 400050, China
[2]School of Applied Science and Technology, Chongqing University of Technology, Chongqing 400050, China
[3]Department of Physics and Materials Science, City University of Hong Kong, Hong Kong

*Corresponding author, email paul.chu@cityu.edu.hk

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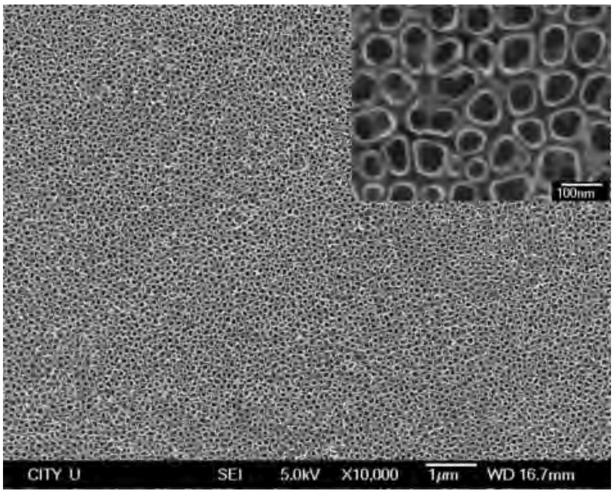


1 Surface morphologies of TiO_2 nanotubular layer formed on Ti by anodisation in 0·5 wt-% HF at 15 V

prepared specimens was observed through a scanning electron microscope (JSM-6700F, JEOL).

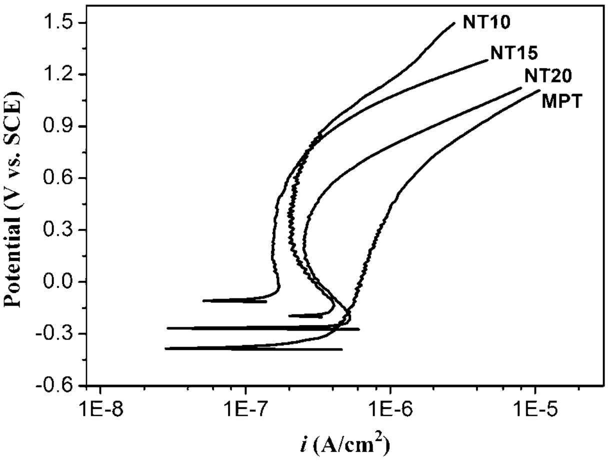
Corrosion tests

The electrochemical experiments were performed on a classical three electrode system in artificial saliva[2] containing 5 g L^{-1} BSA, maintained at $37\pm1^\circ$C using a Zahner Zennium electrochemical instrumentation system.

Potentiodynamic polarisation tests were conducted at a scanning rate of 0·1 mV s^{-1} after dipping the specimen into the electrolyte for 10 min. The electrochemical impedance spectra (EIS) were measured from 10 mHz to 10 kHz with a voltage perturbation amplitude of 10 mV in triplicate without aeration. Before the impedance measurement, the specimen was kept floating at the selected potential values from activation to passivation regions for each impedance spectrum. The EIS spectra were fitted with the ZSimpWin software.

Results and discussion

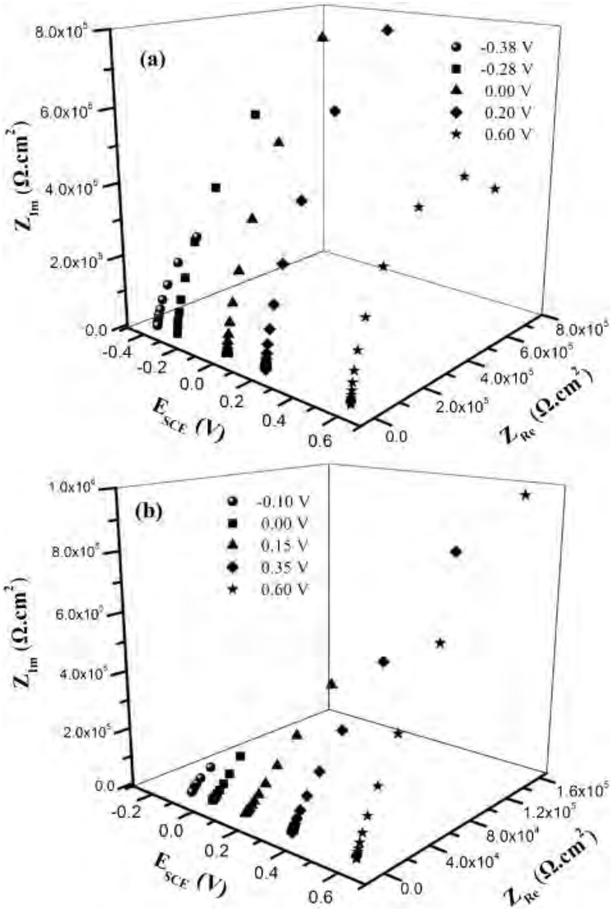
Figure 1 shows the highly ordered nanotubular layers prepared by anodisation of titanium at a voltage of 15 V in 0·5 wt-% hydrofluoric acid. The diameter of TiO_2 nanotube is 39 ± 7 nm at 10 V, $59\pm8{\cdot}7$ nm at 15 V, and $86\pm12{\cdot}6$ nm at 20 V respectively.



2 Anodic polarisation curves obtained from mechanically polished and nanotubular titanium samples in artificial saliva with 5 g L^{-1} BSA

Figure 2 indicates the potentiodynamic polarisation curves obtained in artificial saliva containing 5 g L^{-1} BSA. After a 10 min immersion, the corrosion potential E_{corr} for MPT samples was more negative than those of nanotubular titanium. The MPT surface exhibited rapid passivation behaviour, but for the nanotubular titanium, there existed an obvious transition region from activation to passivation. Su and Zhou[11] reported the anodic TiO_2 nanotube had a double layer wall. Once the aggressive ions penetrate into the space, it may result in the quick dissolution of the outer layer of TiO_2 nanotubes and the reformation of oxide,[11] which may cause the transition region from activation to passivation. In addition, albumin may align itself on titanium surface through two metal-cation binding sites, the N terminus and the free cysteine, Cys-34, and then the triangular albumin molecule with equilateral 8 nm sides transforms to a flattened triangular shape with 13 nm sides.[12] The diameter of TiO_2 nanotube exceeds 13 nm. The albumin molecule could infiltrate into the TiO_2 nanotube, which might inhibit the transfer of ions into the interior of the TiO_2 nanotube or the kinetics of charge transfer reactions.[13] Therefore, the variations of anodic polarisation curves of MPT and NT samples might be attributed to a rapid and effective surface blockage of the nanotubular surface. Moreover, the passivation current density for the nanotubular samples was lower than that of the bare titanium.

Padilla and Bronson[13] reported that the increasing potential enhanced the adsorption of albumin. In order



3 Nyquist plots of *a* mechanically polished and *b* nanotubular titanium in artificial saliva with 5 g L^{-1} BSA at selected potentials

Table 1 Fitted results from Nyquist plots from MPT and NT15 samples in artificial saliva with 5 g L^{-1} BSA

Test samples	Potential	$R_S/\Omega\ cm^2$	$Q_1/\mu F\ cm^{-2}$	n_1	$R_1/\Omega\ cm^2$	$Q_2/\mu F\ cm^{-2}$	n_2	$R_2/\Omega\ cm^2$
MPT	−0·38	77·8	34·3	0·9	$5{\cdot}04\times10^5$	…	…	…
	−0·28	78·5	17·5	0·93	$1{\cdot}39\times10^5$	…	…	…
	0	78·6	12·1	0·94	$1{\cdot}73\times10^6$	…	…	…
	0·2	78·6	9·87	0·95	$1{\cdot}79\times10^6$	…	…	…
	0·6	79·1	7·75	0·96	$9{\cdot}95\times10^5$	…	…	…
NT15	−0·1	80·3	234	0·87	$6{\cdot}89\times10^5$	165	0·81	$3{\cdot}17\times10^2$
	0·0	80·1	52·3	0·83	$3{\cdot}12\times10^5$	56·7	0·89	$3{\cdot}87\times10^2$
	0·15	80·5	19·5	0·93	$3{\cdot}25\times10^6$	43·2	0·97	$2{\cdot}38\times10^3$
	0·35	81·1	13·7	1·00	$4{\cdot}67\times10^6$	37·6	0·89	$4{\cdot}35\times10^4$
	0·6	81·3	41·2	1·00	$2{\cdot}85\times10^6$	74·4	0·94	$6{\cdot}31\times10^6$

to investigate the interactions of albumin with the MPT and nanotubular sample surface, the EIS was measured at selected potentials from activation to passivation region. The EIS results are depicted in Fig. 3. The simulation results are listed in Table 1. For the MPT sample, we used $R_s(R_1Q_1)$ equivalent circuit to fit the impedance spectra. The effective capacitance (Q_1) results from the contributions of the oxide capacitance and the adsorption of albumin.[11,14] Compared to MPT sample, the Nyquist plots for NT15 sample consisted of one high capacitance loop and one low frequency capacitance loop. The equivalent circuit $R_s(R_1Q_1)(R_2Q_2)$ was used, the components of which are resistance and the constant phase element (CPE) of the interbarrier layer (R_1 and Q_1, respectively), resistance and CPE of the outer nanotube layer and the adsorption layer of albumin (R_2 and Q_2 respectively). The CPE also represented a shift from the ideal capacitive behaviour. The chi-squared values on the order of 10^{-4} indicate excellent agreement between the experimental and modelled values, and the experimental error is lower than 10%. At E_{corr} (−0·38 V for MPT sample and −0·10 V for NT15 sample), a highly capacitance loop was shown; however, the phase angles from medium to low frequencies were lower than −70°, suggesting that anodic reaction happened on both tested samples. As the applied polarisation potential became more positive, but not over 0·4 V, the diameter of the capacitance loop increased, indicating that the growing corrosion products began to cover the MPT and NT15 sample surface gradually. The adsorption of albumin could render the variations of the capacitances with increasing polarisation potentials.[14] For the MPT sample, the magnitude of Q_1 values ranged from 34·3 to 7·75 $\mu F\ cm^{-2}$ as the applied potential becomes less negative. The reason may be that the fractional coverage of adsorbing albumin approached unity and served as a barrier against the aggressive ions. Meanwhile, the R_1 value increased slowly. For NT15 sample, the changes for R_1 and Q_1 values were similar to those of MPT sample with increasing potential in the positive direction. A higher value of R_1 can be observed in Table 1, suggesting an emphatic resistive behaviour of the inner oxide layer. The obvious changes in R_2 and Q_1 values can be seen as the applied potential was progressively less negative. Several earlier studies have indicated that the outer nanoporous layer had lower impedance.[7,8] Therefore, the increase in R_2 value and the decrease in Q_1 value may be attributed to the adsorption of BSA. It is known that the increasing potential was beneficial to the adsorption of albumin.[13] When the coverage ratio of adsorbed albumin on the outer TiO_2 nanotube layer gradually increased and approached unity, it may even provide an effective barrier against the in-leakage of aggressive ions, the oxygen evolution reaction and the charge transfer responsible for the outer TiO_2 nanotube hydroxylation.

Conclusions

We found that titanium with TiO_2 nanotube layer showed higher corrosion resistance than that of the mechanical polished titanium in artificial saliva containing 5 g L^{-1} BSA. The addition of BSA had greater influence on the corrosion behaviour of the former. The higher surface area was beneficial to the adsorption of BSA, which enhanced corrosion resistance of the outer TiO_2 nanotubular layer.

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