Improvement the corrosion Behavior of Titanium by Nanotubular Oxide in a simulated saliva solution

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Abstract. The corrosion behavior of Titanium in a simulated saliva solution was improved by Nanotubular Oxide via electrochemical anodizing treatment using three electrodes cell potentiostat at 37°C. The anodization treatment was achieved in a non-aqueous electrolyte with the following composition: 200mL ethylene glycol containing 0.6g NH4F and 10 ml of deionized water and using different applied directed voltage at 10°C and constant time of anodizing (15 min.). The anodized titanium layer was examined using SEM, and AFM technique.

The results showed that increasing applied voltage resulted in formation titanium oxide nanotubes with higher corrosion resistance (more positive value of the corrosion potential). The results revealed that good adhered well-ordered vertically aligned titania nanotubes with inner tube diameter of 82nm an mean length of 3microns could be obtained at 30VDC. Low corrosion current density (579 nA.cm-2) and corrosion potential equal to (-209 mV) were observed for untreated titanium metal while a dramatic fall down of the corrosion current was observed for nanotubes TiO2 (76 nA.cm-2) and more positive value of corrosion potential (-138 mV) was observed revealing good corrosion resistance of the improved titanium in saliva solutions.

Keywords: saliva solution, titanium, titanium oxide, corrosion resistance, nanotubes

1. Introduction

In recent years, rapidly increase in the demand of appropriate materials for biomedical applications was happened due to the improving of health care and increasing the longevity of people. Titanium and its alloys are identified as highly biocompatible materials. They are used as the most valuable materials for orthopedic (osteosynthesis plates, articular prostheses, and screws) and dental applications (crown and bridge) [1]. They have attractive bulk mechanical properties like high strength to weight ratio, low modulus of elasticity, outstanding resistance of corrosion, ion releasing at low rate in combination with higher biostability, and a high degree of biocompatibility [2, 3].
Titanium and its alloys display very good resistance of corrosion in several media: alkali, acid, and organic compounds. This outstanding resistance is caused by formation naturally passive oxide film on the surface of titanium and its alloys when they are in contact with air or different aqueous media. The long-term stability of the oxide film in biological environments and the electrochemical properties combined with physicochemical properties of this film are the essential parameter for biocompatibility of titanium or its alloys. The metallic ions released by the implant results in an adverse body reaction to the implant. The quantity of these ions is governed by the corrosion rate. For this reason, many studies on the passivity and corrosion of implants in different aqueous or non-aqueous solutions which simulate fluids of human body such as phosphate-buffered saline solution [4, 5], Ringer’s solution [6,7], artificial saliva [8,9], Hank’s solution,[8,10] have been achieved.

To enhance the corrosion resistance of titanium, various enhancing treatments were performed. This was achieved either by addition of elements such as palladium to improve the cathodic reaction via raising the cathodic polarization curve above the critical active anodic curve in the passive region at higher potentials [11], or by formation of TiN via nitration where nitrogen is introduced in the first μm of the surface leading to increase the corrosion resistance. [12,13]. In spite of these methods are efficient, they are expensive and difficult to accomplish as well other techniques of surface coating, such as chemical vapor deposition and plasma spraying or vacuum plasma spray coating [14]. For this reason, treatments that act on the naturally formed passive layer are preferred.

In recent years, nanotechnology methodology finds increasing interest in the investigators to enhance the corrosion behavior of biomaterials. Nanomaterial formulations have been proved to give large real surface area in comparison with traditional materials [15], which may potentially improve the corrosion resistance of Nano-implants [16, 17]. In this field, Titanium oxide nanotubes have attracted widespread attention because of charge-transport properties, and low electron recombination in addition to their large surface area, hence they are adopted as excellent chemical materials due to formulation of one-dimensional channels for carrier transport. They are of significant interest for applications in the field of water photolysis [18], photocatalysis [19], gas sensors [20], remediation of organic pollutants [21], solar energy cells [22], and recently biomedical and dental implant materials [23].

There are several syntheses methods for preparation of titanium oxide nanotubes such as sol–gel method [24], hydrothermal synthesis [25], template synthesis [26], ion-beam synthesis [27], evaporation [28], and anodic oxidation [29]. Among these, anodic oxidation is extensively used because of its simplicity, low cost approach, controllable and reproducible. This method has the ability to control the size and shape of nanotubes to any required dimensions. Furthermore, a strong adherent titanium oxide nanotubes layer on the surface of a substrate can be achieved by this method which is essential for several practical applications [30]. In the anodizing process, electrolytes containing fluoride, such as HF electrolytes, chromic acid-HF mixtures, (NH₄)₂SO₄-NH₄F mixtures, H₂SO₄-HF mixtures and H₃PO₄-NaF mixtures have been used for preparing self-organized nanotubular titanium oxide [31-34].

The present work was undertaken to prepare Titanium oxide nanotube by anodizing in non-aqueous electrolyte and study its corrosion behavior in comparison with commercially pure titanium in a new simulated saliva solution.

2. Experimental work

2.1. Preparation of TiO₂ nanotube layer
Titanium thin foils having thickness of 0.25 mm and a purity of 99.5% (Alfa Aesar) were used to prepare the samples. These substrates were fabricated in circular shapes with 2.5 cm diameter, then polished by SiC emery paper with grit size no 1200, degreased with acetone, washed distilled water, and finally with ethanol. To prepare Titanium oxide nanotubes, titanium substrate was submerged in a mixture consist of 100 ml deionized water, 3 ml 70% HNO₃, and 2 ml 48% HF for 5 min to remove titanium oxide layer, then rinsed in deionized water and dried under a hot stream of nitrogen. Anodization was performed by two electrodes configuration where the treated titanium substrate was used as anode (working electrode) and platinum sheet was used as cathode (counter electrode). Two copper clips were used to clamp the two electrodes in parallel and the distance between electrodes was fixed at 20 mm. The anodization was achieved using an electrolyte composed of 200 ml ethylene glycol (99.8%, BDH), 10 ml of deionized water (0.2Ms.cm) and 0.6g of NH₄F (99.8%, BDH) under different applying DC voltage(15, 20, 25, and 30V) for 15 min at a temperature of 10°C. The value of the applied voltage was chosen based on the observations of the previous studies which reported that anodizing of Ti at 10 V in ethylene glycol containing 0.5 wt% ammonium fluoride and 2.5 wt% of water didn’t give any distinct nanotubes [35]. Also increasing applied voltage higher than 30V results in increasing of bath temperature leading to increase the chemical dissolution of the oxide. These observations confirmed that a minimum potential higher than 10VDC is required for the formation of self-organized nanotubes [36]. A power supply model UNI-T: UTP1303 (0-32V/0-3A) was used in the anodizing treatment. After anodizing, the samples were rinsed with deionized water and dried in hot stream of nitrogen. The microstructures of nanotube layers were observed by Field emission scanning electron microscope (Hitachi FE-SEM model S-4160, Japan) and Atomic Force Microscope (AA3000, Angstrom Advanced Inc., USA). By observing mechanically fractured samples, a cross section photograph was obtained.

2.2. Corrosion test preparation

For corrosion study, commercially pure titanium substrate and titanium oxide nanotubes substrates prepared at different applied voltage were used as test specimens. Electric conduction paste with copper was used for mechanical and electrical contacts between the sample and the copper wire. All specimens were carefully mounted with cold epoxy resin. Potentiodynamic polarization was carried out in a simulated body saliva solution with chemical composition shown in Table 1. The electrochemical system consists of computerized advanced potentiostat (type Mlab 200, Germany), and standard three electrodes double wall Pyrex glass of (1L) capacity corrosion cell. Chiller device was used to control the temperature of the solution at 37 ±1°C. All potentials were measured with respect to saturated calomel electrode (SCE) as the reference electrode and a platinum rod was used as a counter electrode. The solution was deaerated for 30 min using high purity nitrogen gas. The test was conducted at a scanning rate of 5 mVs⁻¹. The experiments were performed at pH 7.4.

Table 1 Chemical composition of the simulated saliva solution.

| Compound   | Na₂HPO₄ | NaHCO₃ | CaCl₂ | H₂O    |
|------------|---------|--------|-------|--------|
| Concentration g/l | 0.426 g | 1.68 g | 0.147 g | 800 ml |
3. Results and discussion

3.1 Corrosion behavior

Figure 1 shows the typical potentiodynamic polarization curve for commercially pure titanium substrate and titanium oxide nanotubes substrates prepared at different applied voltages in the proposed simulated Saliva solution. Also further experiment was achieved at constant applied voltage 30V and increasing time up to 30min. Table 2 shows the values of corrosion current densities and the corresponding corrosion potentials. The results showed that the corrosion potential of commercially pure titanium was -209.2 mV vs. SCE and its corrosion current density was 578.98 nA.cm⁻². The corrosion resistance of titanium in the present saliva solution is good as a result of existing the protective and naturally self-adherent titanium dioxide film with thickness of 2–6 nm [37, 38]. However, the corrosion resistance in the present work is lower than that observed at other saliva solutions due to the effect of chloride ions where TiO₂ becomes unstable and easy to hydrolyze [39]:

$$\text{TiO}_2^+ + \text{Cl}^- + 2\text{H}_2\text{O} \leftrightarrow [\text{Ti(OH)}_3]\text{Cl} + \text{H}^+$$

This hydrolysis step led to decrease the pH to less than 6.5.

A dramatics fall down of the corrosion current was observed for Titanium oxide nanotube samples prepared at different applied voltage with corrosion potentials became more positive values as shown in table 2. Similar behavior was observed by Yang et al.[40] where they found that increasing applied voltage of anodizing the titanium resulted in shifting the corrosion potential to more positive values in the 3.5 wt% NaCl solution. Asumpinwong et.al [41] in their work on the corrosion of anodized Ti-6Al-4V alloy in a 0.9% saline solution found that the corrosion potential increased with increased anodized voltage. At applied voltage of 30VDC, Titanium oxide nanotube substrate has the lowest corrosion current density (76 nA.cm⁻²) and more noble value of corrosion potential (-138 mV vs. SCE). Using anodizing time 30min led to a slightly change in the corrosion potential and corrosion current density as shown in Table 2 with excessive heating of the anodizing solution hence it is preferred to consider the applied voltage of 30V and anodizing time of 15min as the best operating conditions for anodizing of titanium.

The very low corrosion current density of the prepared nanotubular titanium oxide confirming no pitting corrosion can be occurred [42]. The enhanced corrosion resistance of the anodized titanium may be attributed to relatively thick oxide layer formed during anodizing at the substrate/nanotube interface, therefore the prepared titanium oxide nanotube can be utilized for different medical applications due to the best corrosion resistance it has.
Fig. 1. Potentiodynamic polarization plots of commercially pure titanium and titanium oxide nanotubes prepared at different applied voltage in the simulated saliva solution

Table 2 corrosion parameters for titanium and titanium oxide nanotube substrate

| Substrate                  | Conditions     | Corrosion potential (E(mV vs. SCE)) | Corrosion current density (μA/cm²) |
|----------------------------|----------------|------------------------------------|-----------------------------------|
| Titanium                   | ------         | -209.2                             | 0.579                             |
| Titanium oxide nanotube    | 15V, 15 min.  | -171                               | 0.10                              |
| Titanium oxide nanotube    | 20 V, 15 min. | -162                               | 0.09                              |
| Titanium oxide nanotube    | 25 V, 15 min. | -145                               | 0.08                              |
| Titanium oxide nanotube    | 30 V, 15 min. | -138                               | 0.076                             |
| Titanium oxide nanotube    | 30 V, 30 min. | -130                               | 0.066                             |

Yu et al. [43] investigated the corrosion behaviors of TiO₂ nanotube layers on titanium in Hank’s solution \{NaCl (8 g.l⁻¹), KCl (0.4 g.l⁻¹), CaCl₂ (0.14 g.l⁻¹), NaHCO₃ (0.35 g.l⁻¹), Na₂HPO₄·2H₂O (0.06 g.l⁻¹), MgCl₂·6H₂O (0.1 g.l⁻¹), KH₂PO₄ (0.06 g.l⁻¹), MgSO₄·7H₂O (0.06 g.l⁻¹) and glucose (1.0 g.l⁻¹)\}. TiO₂ nanotube layers were prepared by anodizing in a 0.5 wt% HF solution at 20 V for 1 h. They found that TiO₂ nanotubes have a corrosion...
potential of ~277 V vs. Ag/AgCl with corrosion current density of 77 nA.cm$^{-2}$. Liu et al. [44] investigated the corrosion behavior of titanium oxide nanotubes in artificial saliva with composition: 0.4 g.l$^{-1}$NaCl, 0.9 g.l$^{-1}$KCl, 0.795 g.l$^{-1}$ CaCl$_2$.2H$_2$O, 0.69 g.l$^{-1}$ NaH$_2$PO$_4$, 1 g.l$^{-1}$ urea and pH adjusted to 5 by lactic acid. TiO$_2$ nanotubes were prepared by anodizing for 30 min in 0.5 wt. % hydrofluoric acid. They found that titanium nanotubes prepared at 15VDC has the lowest anodic corrosion current density at -0.4 V vs. SCE, which is about 2.6×10/g2377A.cm$^{-2}$.

Al-Swayih[36] prepared Nanotube titanium oxide using anodization technique in 1M H$_3$PO$_4$ + 0.8 wt.% NaF, and tested in Hank's solution{NaCl (8.00g), KCl(0.40g), CaCl$_2$(0.19g),NaHCO$_3$(0.35g),Na$_2$HPO$_4$(0.06g),MgCl$_2$.6H$_2$O(0.19g),MgSO$_4$.7H$_2$O (0.06g) and Glucose (1.00g)}. He found that the best corrosion resistance was obtained in anodizing voltage of 30V for 30 min where its corrosion potenatial was -0.442 V vs. SCE, and its corrosion current was 6.67 µA.cm$^{-2}$.

Rafieerad et al. [45] studied the corrosion behavior of self-organized TiO$_2$ nanotubes coated on Ti–6Al–7Nb alloy in simulated human blood fluid. TiO$_2$ nanotubes having an average inner diameter of 160 nm were prepared by anodizing in electrolyte composed of sodium fluoride dissolved in a 90:10 ethylene glycol and distilled water solvent at a constant potential of 60 V for 5 h. They found that TiO$_2$ nanotubes has a corrosion potential of -0.358V vs. SCE and corrosion current density of 7.96µA.cm$^{-2}$.

The comparison of the present work with the above mentioned works shows that the prepared titanium oxide nanotube has corrosion potential more noble value and lower corrosion current density. The differences in the corrosion behaviors of titanium oxide nanotubes in various simulated body fluid solutions are resulted from the variation in the microstructure of the surface oxide layer which depends on the anodizing parameters. Previous studies reported that the electrochemical corrosion behavior of nanotubular titanium oxide depends entirely on the diameter and length of the nanotubes in addition to the thickness of the barrier layer [36, 44]. The variation in the methods used for treatment the surface of substrate before anodizing may also lead to different microstructure of the oxide nanotube. Besides, an essential factor is the characteristics of the electrolyte used in the anodizing process [46].

3.2 Surface characterizations

The surface morphology and topography of titanium substrates were examined using SEM and AFM. The surface morphology of commercially pure titanium is shown in fig 2. It was observed there are no distinct features on the surface of commercially pure titanium and having a rough surface and some naturally formed protective barrier oxide. The surface morphology of Ti foil anodized at 30 V for 15 min at a temperature of 10°C is shown in Fig. 3. The results show highly ordered nanotubular layers, revealing a uniform and regular structure. The resulted nanotubes had a diameter of about 80 nm, and a length of about 3µm, While AFM images presented in Fig. 3c show approximately tube diameter around (85nm).
Fig. 2 SEM (a-) and AFM (b-2D, c-3D) images of the surface of commercially pure titanium
4. Conclusions

Improving the corrosion behavior of commercially pure titanium can be achieved via electrochemical anodizing treatment. The very low corrosion current density obtained for the prepared titanium oxide nanotube substrate tested in the proposed artificial saliva showing that it is passive in this electrolyte. In comparison with the previous works, the present work gives more interesting results with respect to the properties of the prepared nanotubes TiO₂ (more corrosion resistance). This comparison showed that the morphology and surface properties of the oxide film are the essential factors affecting on the corrosion behavior of titanium oxide nanotube in simulated body fluids. Consequently, these surface properties depend strongly on the factors of the anodizing process. The present study confirmed that titanium with nanotubes could improve the corrosion resistance in biomedical applications.

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