The corrosion behaviour of Pt modified TiO_2 biomaterials in vitro conditions

Başak Doğru Mert, Seyran Gündüz, Özlem İşler, Birgül Yazıcı

Çukurova University, Science and Letters Faculty, Chemistry Department, 01330 Balcalı, Adana/ Turkey

Abstract

Titanium and its alloys have been widely used for biomedical applications due to high biocompatibility, osseointegration and corrosion behaviour. Therefore, investigation and enhancing the corrosion behavior of these materials have vital importance. In this study, the corrosion performance of Ti enhanced via anodizing and Pt deposition, and we investigated the biomedical application of this modified Ti (Ti/TiO_2-Pt) in vitro conditions. In anodizing procedure, titanium oxide (**(**TiO_2) layer was occurred on Ti surface at 17.5 V during different anodizing times in 0.1 M HF solution. Then Pt deposited on Ti/TiO_2 by galvanostatically (100 μg Pt per cm^{-2}). The biocompatibility and corrosion behaviour of Ti, Ti/TiO_2 and Ti/TiO_2-Pt were investigated with the help of cyclic voltammetry, and polarization measurements in physiological saline solution at 310 K. The surface morphologies were determined with surface photographs and scanning electron microscopy (SEM) images, furthermore the contact angles of bare and modified surface were investigated. The corrosion rate was determined during long immersion period. Results showed that the anodizing process and Pt deposition procedures increased the corrosion resistance of Ti. The lower anodic current density, contact angles and higher corrosion resistance were determined for Ti/TiO_2-Pt. This is illustrated with the produced more stable, compact film on the surface.

Keywords: Biocompatibility; anodizing; physiological saline; corrosion

1. INTRODUCTION

Titanium implants are used in a great variety in the human body as an implant materials, because they show high corrosion endurance due to the oxide film developing even at room temperature. This oxide film gives chemical stability and biocompatibility to the material. Although there are many commercial titanium compounds, pure titanium is the most utilized form at biomedical applications. These materials have been evolved to not react with tissue fluids so that they will not deform, expand or corrode [1-12]. Corrosion happens when metals and its compounds react with their environment chemically or electrochemically and get degraded and damaged by forming oxides, hydroxyl oxides and other compounds. More importantly, these corrosion products can penetrate into tissues damaging the human cells. As it known, human body consist of water, soluble oxygen, proteins and various ions like chloride, hydroxide and etc. For this reason, the human body is an extremely corrosive environment for the metals used as biomaterials. This corrosive environment reduces the strength of metals. One of the solutions for preventing corrosion of these metals is coating these materials with corrosion-resistant oxide layer [10-13]. Although there are many oxidizing methods available, the most practical and cost efficient one is the anodizing procedure. Apart from augmenting corrosion resistance, the other important benefits of coating titanium and its compounds with oxide layer are, this procedure also increases biocompatibility and has some osteogenetic effects [12,14].

In this study, we researched the electrochemical behaviours of titanium (Ti), Ti/TiO_2 (formed by the anodizing method at separate durations) and Ti/TiO_2-Pt by electrochemical methods in physiological saline solution.

2. Experimental

A cylindrical titanium with 0.785 cm^2 of the surface area (Ti, 99.9%) rods cut to 2 cm length of titanium rod, used as working electrode. The electrical conductivity was provided by a copper wire. The surface of electrode was smoothed by emery paper down to 1200 grade. Then, it was cleaned by acetone/ethanol mixture and pure water. Titanium oxide was prepared by electrochemical anodizing method in 0.1 M HF solution with two electrode technique help with Matrix power supply (MPS-3003L-3) instrument. In this system, a platinum sheet (with 2 cm^2 surface area) was used as the counter electrode. The 17.5 V obtained the system for different process times (30 and 45 minutes). Then Pt deposited on Ti/TiO_2 by galvanostatically (100 µg Pt per cm^{-2}). The SEM images were taken using a Carl Zeiss Evo 40 SEM instrument at high vacuum and 10 kV EHT. The contact angle of water for bare and anodized Ti electrodes were taken using Theta Lite Optical Tensiometer. The corrosion measurements were carried using by CHI 604D A.C. electrochemical analyzer at 310 K, open to atmosphere. A platinum sheet (with 2 cm^2 surface area) was used as the counter electrode and Ag/AgCl (3 M KCl) electrode was used as the reference electrode. The corrosion performance of electrodes were investigated in physiological saline (0.9% NaCl) solution. The polarization curves were potentiodynamically obtained with a scan rate of 1 mV s^{-1}. The cyclic voltammetry measurements (CV) were obtained in the potential ranges between −0.5 V and 2.5 V with a scan rate of 0.1 V s^{-1}.

3. RESULTS AND DISCUSSION

3.1. Preparation of Ti/TiO_2 and Ti/TiO_2-Pt

Our previous study has identified that most convenient anodizing potential is 17.5 V [13]. During anodizing procedure, Ti oxidized to (Ti^{2+} TiO_2^{2+}, Ti^{3+},etc.) hydroxide and/or oxide forms $(Ti(OH)_4$ and/or TiO_2 then with the help of F^- ions dissolution is continued according to following equations;

$$TiO_2 + 6F^- + 4H^+ \rightarrow TiF_6^{2-} + 2H_2O \quad (1)$$

$$Ti(OH)_4 + 6F^- \rightarrow 4OH^- + TiF_6^{2-} \quad (2)$$

Initially, the surface is completely opened and cleaned by the effect of solution and the new surface layers (TiO_2, $Ti(OH)_4$) will be created depending on the period of application [13]. These layers'conductivity and surface morphology have a great importantance for biomedical applications. The related experimental results for different operation times are presented in Table 1. As seen from Table 1, the structure and character of oxide layer are deeply illustrated with anodizing time. The stable and conductive oxide forms are observed as 30 and 45 minutes (Ti/TiO_2(30) and Ti/TiO_2(45)). The conductivity values are 1.85 x 10^4 and 1.41 x10^4 S cm^{-1} for Ti/TiO_2(30) and Ti/TiO_2(45), respectively. The surface of these electrodes are violet and grey which are defined by a Pourbaix as a TiO_2 and Ti_2O_3 have violet and very stable [13].

Table 1. The conductivity and surface colour of TiO_2 for different anodizing periods.

Anodizing time min.	Conductivity of TiO_2 S cm^{-1} ($x10^4$)	Surface Colour
15	1.32	
30	1.85	
45	1.41	
60	0.10	

3.2. SEM micrographs

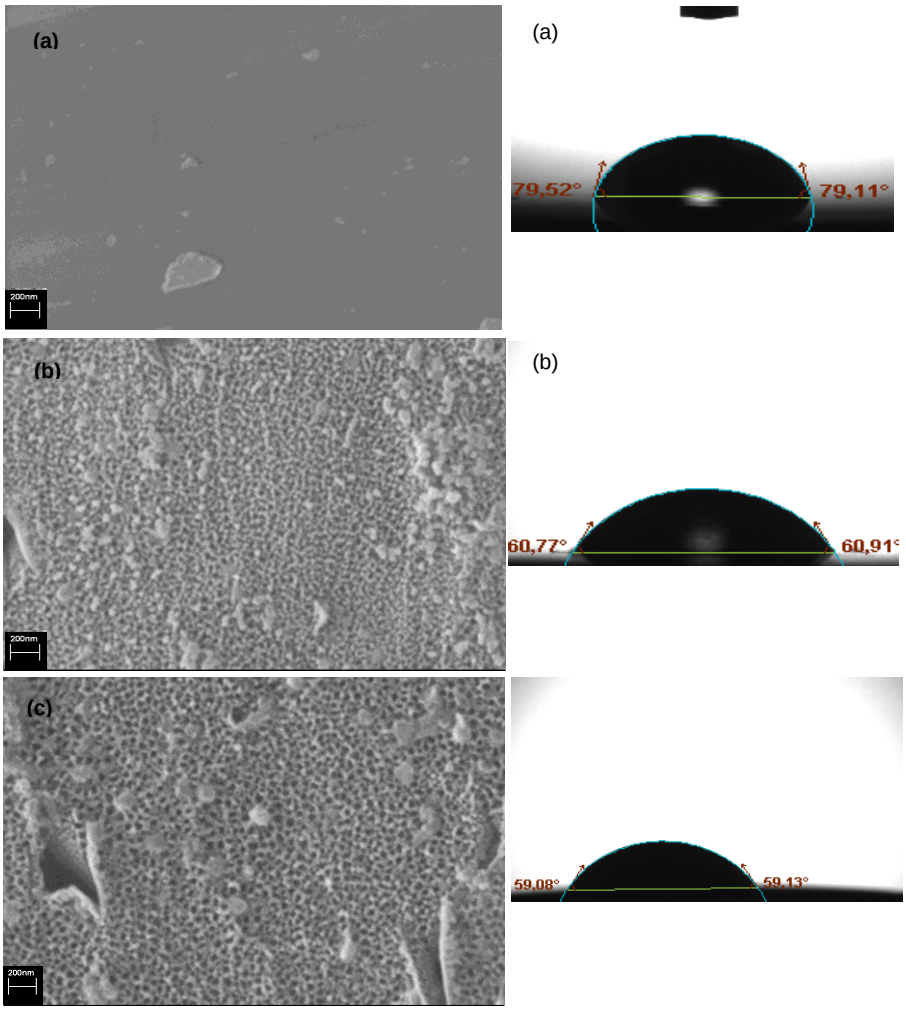


Figure 1: The surface analysis (SEM micrographs and contact angles) of Ti (a), Ti/TiO_2 (30) (b), Ti/TiO_2 (45) (c).

In Figure 1a, the scanning electron microscope (SEM) micrograph of bare titanium surface is demonstrated. As seen in Fig. 1a, the electrode surface is smooth, only sanding trails are observed. In Fig. 1b and c present $Ti/TiO_2(30)$ and $Ti/TiO_2(45)$ surfaces respectively. The oxide films were produced carefully on electrode surfaces and nanopores were dispersed homogenously. The $Ti/TiO_2(30)$ had better surface morphology than $Ti/TiO_2(45)$ electrode. It has lower pore diameter than $Ti/TiO_2(45)$. Fig 2 shows that processing time is increased and the surface deformation occurs at 45th min. Chang et. all [14] showed that the morphology of the nano structure also plays a very important role in the biocompatibility of titanium. The nanopore morphology enhances osteoblast adhesion, proliferation and accelerates the healing process and promotes bone mineralization. The diameter of Ti/TiO_2 has crucial effect on this [14,15]. The contact angle of water for Ti and anodized electrodes ($Ti/TiO_2(30)$ and $Ti/TiO_2(45)$) are seen Fig. 1. The porous structure of anodized surface decreased the contact angle. The wettability of surface is enhanced via anodizing process. Results showed that anodizing is important surface procedure for producing suitable surface morphology and its wettability. The most convenient surface ise seen as $Ti/TiO_2(30)$ from Fig.1. After Pt deposition on $Ti/TiO_2(30)$ the morphology and contact angle is significantly changed. The related images are seen in Fig. 2. The deposited Pt particles are seen clearly and lower contact angle determined due to high surface roughness of the electrode.

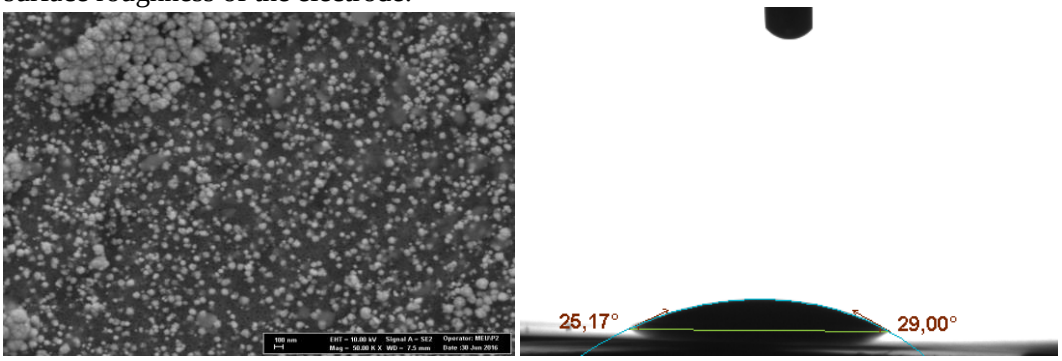


Figure 2: The SEM micrographs and contact angle of Ti/TiO_2 (30) -Pt

3.3. Electrochemical measurements

Fig. 3 shows the cyclic voltammograms of Ti, $Ti/TiO_2(30)$ and $Ti/TiO_2(45)$ in physiological saline solution at 310 K. During forward scan $Ti/TiO_2(30)$ had minimum anodic current density which may illustrate with surface stability and corrosion performance.

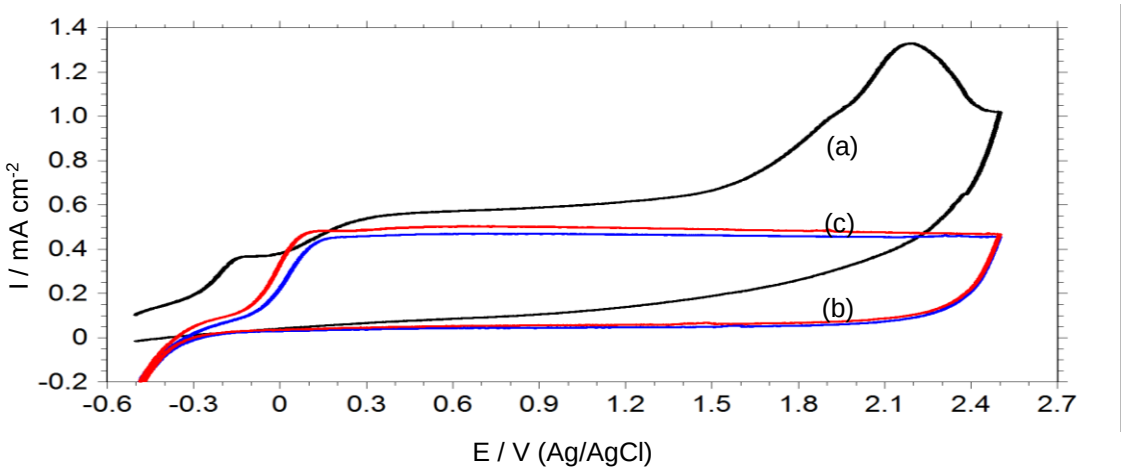


Figure 3. The cyclic voltammogram of Ti (a), Ti/TiO_2 (30) (b), Ti/TiO_2 (45) (c) in physiological saline solution at 310 K (scan rate 100 mV s^{-1}).

In Fig. 4, the cyclic voltammogram of Ti, Ti/TiO_2(30)-Pt and Ti/TiO_2(45)-Pt in physiological saline solution at 310 K are presented. During the scan the most stable, lowest current density values are detected for Ti/TiO_2(30)-Pt electrode.

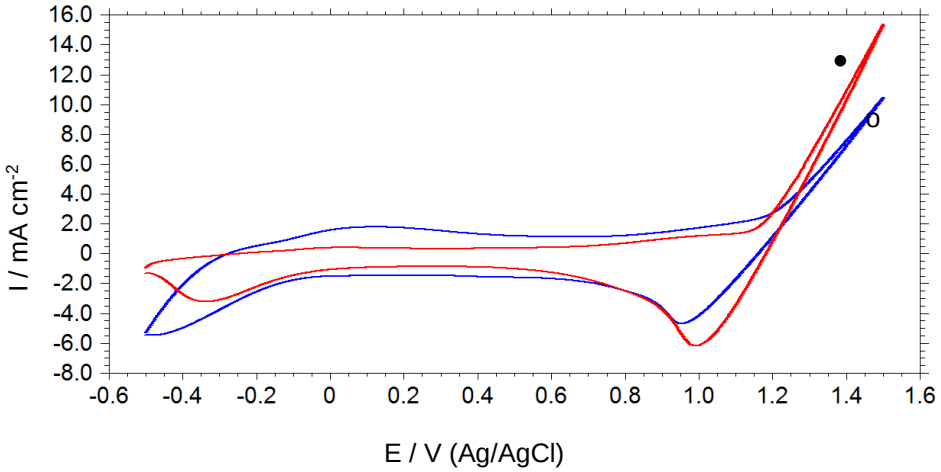


Figure 4. The cyclic voltammogram of Ti/TiO_2 (30)-Pt (o), Ti/TiO_2 (45) -Pt (•) in physiological saline solution at 310 K (scan rate 100 mV s^{-1}).

The anodic polarization measurements of all electrodes were investigated and the open circuit potential (E_{ocp}) values were -0.498 ; -0.319 ve -0.377 V (vs Ag/AgCl) in physiological saline solution at 310 K for Ti, Ti/TiO_2(30) and Ti/TiO_2(45) electrodes respectively (Fig.5).

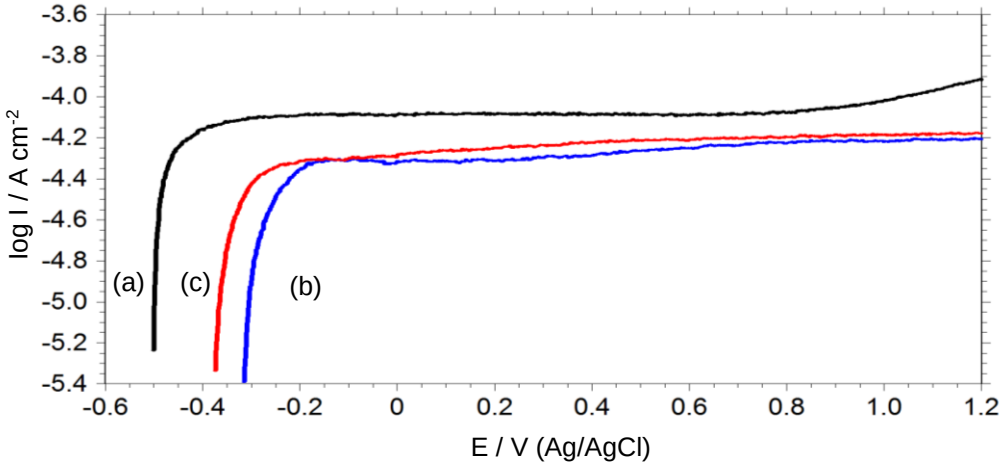


Figure 5. The anodic polarization curves of Ti (a), Ti/TiO_2 (30) (b), Ti/TiO_2 (45) (c) in physiological saline solution at 310 K (scan rate 1 mV s^{-1}).

The shift in E_{ocp} values may relate with oxide stability and morphology. During the anodic scan, the lowest anodic current density was detected for Ti/TiO_2(30), implying better protection efficiency than the others. The polarization curves of Pt deposited electrodes are given in Fig. 6. The comparison of electrodes shows that Pt deposited electrodes has lower current density and higher corrosion performance than bare and oxide coated electrodes.

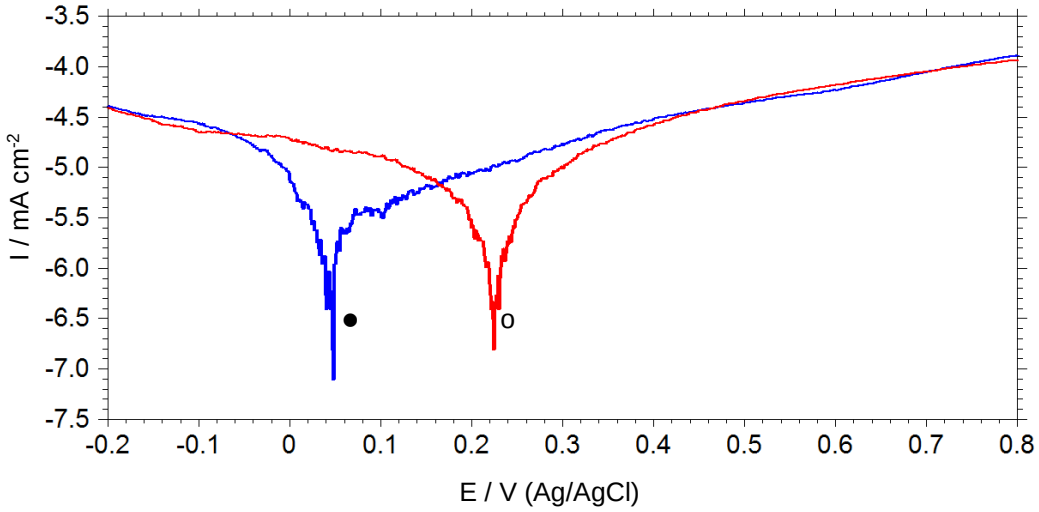


Figure 6. The polarization curves of Ti/TiO_2 (30)-Pt (o), Ti/TiO_2 (45) -Pt (•) in physiological saline solution at 310 K (scan rate 100 mV s^{-1}).

4. CONCLUSIONS

The data on biocompatibility is extremely important for the selection of the biomaterials. Biocompatibility assessment regarding corrosion of these materials should be tested in sample solutions similar to body fluids like; physiological saline solution. The aim of this study is to assist in developing durable biomaterials that doesn't need replacing and can be utilized lifelong. According to the results of our study; Ti/TiO_2 electrodes have been formed homogenously in a 0.1 M HF solution, by using the anodizing process at different process times. In SEM views, the nano-pores diameter varies between 5 - 10 nanometers. The surface morphology of Ti/TiO_2(30) is much more homogenous than Ti/TiO_2(45). According to the cyclic voltammetry and anodic polarization curves; the oxide layer of Ti/TiO_2(30) is more stable and more effective against corrosion in physiological saline at 310 K. Furthermore Pt deposition is enhanced the performance of Ti/TiO_2(30) and Ti/TiO_2 (30)-Pt is exhibited more protective behavior.

5. ACKNOWLEDGEMENTS

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