



Electrochemical and semiconducting properties of thin passive film formed on titanium in chloride medium at various pH conditions



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ABSTRACT

The electrochemical behavior of titanium has been investigated in chloride electrolyte of different pH values (2.1, 5.2 and 7.4). Potentiodynamic polarization studies showed wide passive behavior irrespective of change in pH. Passive films were grown by applying different passive potentials (0.2 to 0.6 V (vs SCE)) by recording chronoamperometric curves for duration of 8 h. Electrochemical impedance spectroscopy (EIS) measurements showed higher impedance values for the oxide layer grown in neutral pH condition and for oxides formed at higher formation potentials. Emphasis is made mainly on the properties of titanium oxide estimated by Mott-Schottky analysis, which shows that passive film formed, is of *n*-type semiconducting film and the donor concentration is in the order of 10^{20} cm^{-3} . The calculated diffusivity of point defects is in the range of $(0.5 \text{ to } 2.5) \times 10^{-16} \text{ cm}^2 \text{ s}^{-1}$ and tends to decrease with increase in electrolyte pH. Surface morphology of the passive films was examined using scanning electron microscope and surface roughness was characterized using confocal microscope. *Ex-situ* ellipsometry measurements were performed to analyze the optical constants of the oxide layer and to determine the oxide thickness. The thickness is in the range of 3.5 to 5.8 nm and comparable to the calculated values.

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1. Introduction

Titanium is a common biomaterial, with a standard reduction potential of -1.60 V (vs SHE). Its superior corrosion resistance is due to the passive film that spontaneously forms on the metal surface in air and oxidizing solutions. In spite of being a very active metal, titanium exhibits high corrosion resistance due to the presence of this oxide film and not due to the properties of bulk Ti [1]. Titanium oxide (TiO_2) has a wide band-gap which is of use in number of applications, including transparent conducting oxides, chemical sensors, biosensors, medical implants, photocatalysis etc. TiO_2 has been investigated extensively as one of the most promising implant materials as growth of oxides by various method leads to variation with modified oxide properties [2]. It has been shown that the oxide structure changes over time upon immersion in bio-electrolyte solutions [3,4]. Due to the high concentration of chloride ions and elevated temperature (37°C), these fluids are highly aggressive for biomaterials.

The corrosion and passivation behavior of titanium and its alloys have been investigated by many researchers in different bioelectrolyte solutions. Al-Mayouf et al. [5] reported that corrosion resistance of titanium and its alloy depends on fluoride concentrations and pH value of

the solution and change in oxide film properties is observed on neutral media. Contu et al. [6] focused on the effect of bovine serum on the electrochemical behavior of titanium and titanium alloys in sulfuric acid and sodium hydroxide solution. They reported that α - β alloy displayed better corrosion resistance in these environments. Takemoto et al. [7] investigated the corrosion behavior of titanium in solution containing fluoride and albumin, and showed that, dissolution of titanium is suppressed via formation of the albumin films. Schmidt et al. [8] reported that the flat band potential and the donor density of the anodic films formed on Ti electrode in McIlvaine buffers are dependent on film formation potential, oxide film thickness and electrolyte pH. Minella et al. [9] analyzed the impedance response of thin film TiO_2 electrodes in different pH environment and they concluded that change in pH has pronounced influence on the electrical properties of the oxide film. The effect of pH on corrosion properties of titanium alloys in physiological solution was investigated by Souza et al. [10] and they did not show tendency to pitting corrosion regardless of pH change. Semiconducting properties of Ti6Al4V was investigated by Pacha-Olivenza et al. [11] and the effect of UV treatment on the electrochemical properties of the oxide were studied. The electrochemical behavior of β -type Ti alloy in simulated body fluid at acidic pH (2.3) was investigated by Tsutsumi et al. [12]. They concluded that reconstruction of passive layer aids in decreasing the corrosion rate. Torres et al. [13] studied impedance behavior of nanostructured titania layers in Ringer physiological solution and concluded that barrier and porous layer of TiO_2

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has three time constants instead of two constants. All these reports [8–13] clearly point out that electrochemical and biological performance of the biomaterial can be influenced by the properties of the passive film, such as stoichiometry, defect density, surface defects and diffusivity.

In this regard, the point defect model (PDM) is considered very useful in obtaining information about the passive film, because it provides a logical description of the growth and breakdown of passive films on reactive metal surfaces at the atomic scale. This model is based on the movement of point defects in an electrostatic field and is proposed to interpret the growth behavior of a passive film on a metal surface under steady state and transient conditions. The migration of oxygen anions or oxide ion vacancies is essential for passive film growth. On the other hand, the diffusion of metal cations or cation vacancies results only in metal dissolution [14]. In general, the mass transport of the passive film growth involves both solid-state diffusion and diffusion through extended lattice-imperfections with one mechanism being dominant at a particular instance of time. The transport properties of point defects can be expressed quantitatively by their diffusivity. The quantitative analysis of the PDM and information about the concentration and transport properties of point defects will help in estimating diffusivity of point defects in the passive film [14]. Jiang et al. [15] studied the passivity of titanium in acidic sulfate solutions using potentiostatic polarization in conjunction with Mott-Schottky analysis and proposed a modified PDM for diffusion-controlled oxide growth. According to this model, the rate determining step of the growth process is assumed to be the lattice diffusion of oxygen vacancies and titanium interstitials. Metikos et al. [16] investigated the anodic film formed on Ni-Ti electrode in 1.0 M acetic acid and found it to be of *n*-type semiconductor with diffusion coefficient of oxygen vacancies value $1.67 \times 10^{-18} \text{ cm}^2 \text{ s}^{-1}$. Much research has been done on the high temperature oxidation of titanium in estimating the diffusion coefficient of oxygen vacancy [17,18] but the oxygen diffusivity data in the ambient temperature condition for anodic oxide film is sparse. Moreover, no inclusive report is available on the electrochemical and semi-conducting behavior of titanium in a solution containing chloride ions in estimating the donor concentrations in conjunction with defect diffusivity at varying pH conditions. Estimating the semiconducting and passive film properties of biomaterial at various conditions is essential criteria for the selection of proper implant material.

Therefore, the objective of this work is to investigate the passivity of titanium in acidic and neutral chloride containing solution for identifying the semiconductor properties of the passive film and to determine the film growth dependence on different applied potentials and electrolyte pH.

2. Experimental methods

2.1. Specimen and solution preparation

Samples of cp titanium (Grade 2 type and also containing O up to a max of 0.25 wt%, N up to a max of 0.03 wt%, C up to a max of 0.08 wt%, H up to a maximum of 0.015 wt% and Fe up to a max of 0.3 wt%) of dimensions of $30 \times 10 \times 3 \text{ mm}^3$ were used in this study. They were polished mechanically to mirror finish, rinsed with deionized water and dried in air. A conventional three electrode cell was used for all the electrochemical measurements. A saturated calomel electrode (SCE) was used as the reference electrode, graphite rod as counter electrode and titanium as the working electrode. The testing medium was chloride containing solution of composition: NaCl = 135.1 mM, KCl = 4.61 mM and CaCl₂ = 4.31 mM. Electrochemical test of the titanium samples was examined in this solution under different pH conditions (2.1, 5.2 & 7.4) at room temperature. This solution was chosen to mimic the body fluid conditions since implants undergo severe pH change for various reasons under chloride environment [10,12]. To avoid contamination, the reference electrode was introduced through a Luggin capillary filled with the test electrolyte. The capillary tip was

brought closer to the working electrode to reduce the IR-drop of the solution. The working electrode was pressed against an O-ring sealing a geometrical area of 1 cm² exposed. Solutions of different pH were prepared by adding small quantities of 1 M HCl or 1 M NaOH. All solutions were prepared from reagent grade chemicals and deionized water.

2.2. Electrochemical measurements

Electrochemical impedance spectroscopy (EIS), potentiodynamic polarization and Mott-Schottky analysis were performed. A Gamry Potentiostat (Reference 600–14,083) controlled by a personal computer and softwares (Gamry Framework and Gamry Echem Analyst) were used for this purpose. All the potential values are quoted with reference to SCE. Potentiodynamic scans were performed in a forward direction at a scan rate of 0.50 mV s^{-1} .

A potential range of +0.2 to +0.6 V (vs SCE) was chosen for potentiostatic film growth to ensure the stability of the passive state. Films were grown at each potential for 8 h to ensure that the system attains steady-state. Prior to the film growth, in each of these cases, the air formed oxide film of the electrode was reduced by holding it at -1.2 V (vs SCE) for 5 min. After each film growth period, EIS measurements were carried out. EIS tests were performed by sweeping the frequency range from 30,000 to 0.01 Hz with an excitation voltage of 10 mV (peak-to-peak). Validity of EIS measurements is analyzed using the Kramer - Kronig (KK) transforms by transforming the real axis into the imaginary axis and the imaginary axis into the real axis using the Gamry Echem Analyst software. Consequently, Mott-Schottky analysis was carried out for anodic films grown at different potentials in the negative direction by sweeping the voltage from formation potential to -1 V (vs SCE) at 75 mVs^{-1} .

2.3. Ellipsometry

Thickness optical measurements were performed ex-situ using a variable angle Woolam Spectroscopic Ellipsometer (2000VI model), equipped with a 50 W Quartz Tungsten Halogen Lamp as the light source and a spectral range of 370 to 1690 nm. The incidence angle used for all measurements was 70°. The optical data were fitted by employing a Zspline single-layer model. The optical properties of an oxide layer are given by its complex refractive index n_c where $n_c = n - ik$ (*n* is refractive index and *k* is extinction coefficient).

2.4. Surface characterization

The surface morphology of the oxide film was examined using a high resolution scanning electron microscope (HR SEM FEI Quanta FEG 200). Confocal microscope (Axio, CSM 700, Zeiss, Göttingen, Germany) with Axio CSM 700 3-D software was used for optical microscopy of the surface. 3-D profiles were measured using an objective of 100× magnification. The vertical resolution was 0.05 μm, and the scanning range was 10 μm. The average surface roughness, *S_a*, was measured using a Z image over an area of 129 μm². Measurements were made in triplicate for each sample preparation and the results are presented as mean value ± standard deviation.

3. Results and discussion

3.1. Potentiodynamic polarization measurements

The potentiodynamic polarization behavior of Ti in the test solutions with different pH is shown in Fig. 1. An equilibration time of 30 min was given for the stabilization of open circuit potential before starting the experiment. It is clear from Fig. 1 that the solution pH has a significant effect on the passive current density. These curves are not symmetrical in the anodic and cathodic branches. Although the polarization curves were very similar, the passive region displayed by the samples showed

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