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Surface-treated commercially pure titanium for biomedical applications: Electrochemical, structural, mechanical and chemical characterizations

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ABSTRACT

Modified surfaces have improved the biological performance and biomechanical fixation of dental implants compared to machined (polished) surfaces. However, there is a lack of knowledge about the surface properties of titanium (Ti) as a function of different surface treatment. This study investigated the role of surface treatments on the electrochemical, structural, mechanical and chemical properties of commercial pure titanium (cp-Ti) under different electrolytes. Cp-Ti discs were divided into 6 groups ($n = 5$): machined (M—control); etched with $HCl + H_2O_2$ (Cl), $H_2SO_4 + H_2O_2$ (S); sandblasted with Al_2O_3 (Sb), Al_2O_3 followed by $HCl + H_2O_2$ (SbCl), and Al_2O_3 followed by $H_2SO_4 + H_2O_2$ (SbS). Electrochemical tests were conducted in artificial saliva (pHs 3; 6.5 and 9) and simulated body fluid (SBF—pH 7.4). All surfaces were characterized before and after corrosion tests using atomic force microscopy, scanning electron microscopy, energy dispersive microscopy, X-ray diffraction, surface roughness, Vickers microhardness and surface free energy. The results indicated that Cl group exhibited the highest polarization resistance (R_p) and the lowest capacitance (Q) and corrosion current density (I_{corr}) values. Reduced corrosion stability was noted for the sandblasted groups. Acidic artificial saliva decreased the R_p values of cp-Ti surfaces and produced the highest I_{corr} values. Also, the surface treatment and corrosion process influenced the surface roughness, Vickers microhardness and surface free energy. Based on these results, it can be concluded that acid-etching treatment improved the electrochemical stability of cp-Ti and all treated surfaces behaved negatively in acidic artificial saliva.

1. Introduction

Dental implants have been widely used to rehabilitate partial and complete edentulous patients [1–3]. Commercially pure titanium (cp-Ti) is the most common material used to fabricate dental implants due to its appropriate mechanical strength and biocompatibility [4–7]. However, it is scientifically known that titanium (Ti) can degrade/corrode when exposed to chemicals such as acid, fluoride and saliva [8–10]. The oral fluids may induce the formation of corrosion cracks at the abutment/implant interface [11]. Besides, the pH around dental implants can vary [8] where certain food such as nuts and milk can alkaline saliva [12]. Sugary foods, some fruits, pickled foods, or even infections, chronic diseases and smoking habits can acidify saliva [12–14] leading to the formation of corrosion products. Barao et al. [9] reported reduced corrosion resistance of machined cp-Ti and Ti—6Al—4V alloy in acidic media.

The process of corrosion can affect the mechanical properties, biocompatibility and function of dental implants, which may lead to their failure [8,15,16]. The abnormal electrical currents produced during corrosion, convert dental implants into an electrode, and the negative impact on the surrounding tissue could be an additional cause of implant failure [16].

Several methods of surface treatment have been suggested, including additional techniques to create projections on implant surface [17–19] as well as subtraction techniques to create pores and pits on implant surface [20–22]. Acid etching has been used for cleaning and decontamination of Ti surface besides changing its physical-chemical properties [23,24]. Prolonged treatment with hydrogen peroxide (H_2O_2) is an alternative for deposition of apatite on Ti surface to improve its bioactivity [25]. A method combining sulfuric acid (H_2SO_4) and H_2O_2 has been suggested to control the chemical deoxidation/

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reoxidation of Ti-based materials and promote a clean surface with a reproducible oxide layer for covalent immobilization of bioactive molecules [26]. Furthermore, the chemical treatment of Ti with H_2O_2 and hydrochloric acid (HCl) is a simple method to provide bone formation, apatite deposition for better osteoconductivity and proliferative abilities [27–29]. In addition, this treatment creates a gel layer of bioactive Ti on complex surfaces [27].

Sandblasting is a common method for treatment of Ti surface that increases the adhesion of osteoblasts in biological environment [30] and improves osseointegration of dental implants. The positive effect of sandblasting was previously associated to an increased roughness on implant surface [31]. However, it was recently suggested that Ti osseointegration also results from negative polarized high electrical charge on material surface [32]. Therefore, the method to combine sandblasting with large particles and acid etching (SLA) has become a common implant surface treatment [33]. Clinically, these implant surfaces created an increased deposition of bone tissue in histomorphometric analysis and high removal torque values in biomechanical studies [28]. In general, modified surface improves the biological performance and biomechanical fixation of dental implants compared to machined surfaces [34,35].

Zhang et al. [36] reported reduced corrosion resistance of sandblasted, and sandblasted and large-grits acid etching (SLA) of Ti—10Cu alloy. Also, Faverani et al. [37] observed poor corrosion behavior of Ti—6Al—4V alloy treated with Al_2O_3 sandblasting. On the other hand, sandblasting associated with oxalic acid etching improves the electrochemical properties of Ti [38].

The role of the different surface treatments on the corrosion behavior of Ti is still under study. There is no study that comprehensively and systematically evaluated the electrochemical stability of several clinically relevant implant surfaces, which mimic the real implants used in patients. Further, the corrosion kinetics of those surfaces investigated in different electrolytes has been weakly explored as well. Therefore, the objective of this study was to investigate the influence of different surface treatment protocols on the electrochemical stability of cp-Ti in artificial saliva (pHs 3; 6.5 and 9) and simulated body fluid (SBF) (pH 7.4). The structural (surface roughness, wettability, surface free energy, crystalline composition of oxides, microstructure, and topography), mechanical (microhardness), and chemical (energy dispersive spectroscopy) properties of cp-Ti were also evaluated. Our research hypotheses were (i) clinically used surface modifications would improve the electrochemical stability and surface properties of cp-Ti, and (ii) the electrolyte types would drive the corrosion behavior of cp-Ti.

2. Materials and methods

2.1. Cp-Ti discs

Cp-Ti discs (grade II) with 15 mm in diameter and 2 mm in thickness (MacMaster Carr, Elmhurst, IL, USA) were divided into 6 groups ($n = 5$) as a function of different surfaces treatment: machined (M group) (control); etched with hydrochloric acid + hydrogen peroxide (Cl group); etched with sulfuric acid + hydrogen peroxide (S group); sandblasted with aluminum oxide (Sb group); sandblasted with aluminum oxide and etched with hydrochloric acid + hydrogen peroxide (SbCl group); and sandblasted with aluminum oxide and etched with sulfuric acid + hydrogen peroxide (SbS group).

2.2. Samples preparation

All discs were polished with sequential grid sandpapers (#320, #400, #600) (Carbimet 2, Buehler, Lake Bluff, IL, USA) in an automatic polisher (EcoMet 300 Pro with AutoMet 250; Buehler, Lake Bluff, IL, USA). The samples were ultrasonically cleaned with deionized water (10 min) and 70% propanol (10 min) (Sigma-Aldrich, St. Louis, MO, USA) and dried with warm air at 250 °C [9].

2.3. Surface treatment protocols

The M group was obtained by mechanical polishing, as previously described in Section 2.2. Samples from the Cl group were etched with a solution containing 0.1 mol/L of HCl and 8.8 mol/L of H_2O_2 (Sigma-Aldrich, St. Louis, MO, USA) at 80 °C during 20 min. Then, the samples were washed with distilled water, oven dried at 50 °C for 12 h, heated with air at 400 °C for 1 h, and cooled in an electrical oven [27]. At the end, the discs were washed with distilled water and vacuum dried. In the S group, discs were washed with toluene (Sigma-Aldrich, St. Louis, MO, USA) and chemically treated with a solution containing equal volumes of H_2SO_4 concentrated (Sigma-Aldrich, St. Louis, MO, USA) and an aqueous solution of 30% H_2O_2 (Sigma-Aldrich, St. Louis, MO, USA) at 25 °C for 2 h. Then, the discs were washed with distilled water and vacuum dried [23,39]. In the Sb group, discs were sandblasted with 150 μm particles of Al_2O_3 (Polidental Indústria Comércio Ltd, Cotia, São Paulo, Brazil) deposited at 50 mm of distance with 90° of angulation using 0.45 MPa pressure during 30 s [33]. Then, the discs were rinsed in ultrasonic tank containing distilled water for 15 min and dried at room temperature (23 °C). For the SbCl and SbS groups, the discs were sandblasted and then acid etched with HCl + H_2O_2 and H_2SO_4 + H_2O_2, respectively.

2.4. Electrochemical test

The electrochemical tests were performed using a potentiostat (Interface 1000, Gamry Instruments, Warminster, PA, USA) for the corrosion measurements in an electrochemical cell made of polysulfone. All measurements were performed on a standardized method of three-electrode cell in accordance with the instructions of the American Society for Testing of Materials (ASTM) (G61–86 and G31–72). A saturated calomel electrode (SCE) was used as a reference electrode (RE), a graphite rod as a counter electrode (auxiliary) (CE) and the exposed surface of cp-Ti disc as a working electrode (WE). A total of 10 mL of electrolyte (artificial saliva or simulated body fluid) was used for each corrosion experiment. The electrolyte temperature was maintained at 37 ± 1 °C and different pH levels of artificial saliva (3; 6.5 and 9) were used to mimic the oral environment and the simulated body fluid (SBF) was used to simulate the blood plasma (pH = 7.4).

The chemical composition for the artificial saliva was KCl (0.4 g/L), NaCl (0.4 g/L), $CaCl_2 \cdot 2H_2O$ (0.906 g/L), $NaH_2PO_4 \cdot 2H_2O$ (0.690 g/L), $Na_2S \cdot 9H_2O$ (0.005 g/L), and urea (1.0 g/L) (8, 46). Different pH values were achieved by adding lactic acid (acidic) or NaOH (basic) in an appropriate amount and evaluated in a pH meter. The composition of the SBF was NaCl (12.0045 g/L), $NaHCO_3$ (0.5025 g/L), KCl (0.3360 g/L), K_2HPO_4 (0.2610 g/L), Na_2SO_4 (0.1065 g/L), 1 M HCl (60 mL), $CaCl_2 \cdot 2H_2O$ (0.5520 g/L), $MgCl_2 \cdot H_2O$ (0.4575 g/L). Tris was used to achieve a pH of 7.4 [40].

The exposed area of the disc was estimated by atomic force microscopy (AFM) analysis for all groups (M = 2.04 cm^2, Cl = 2.31 cm^2, S = 2.32 cm^2, Sb = 2.44 cm^2; SbCl = 2.47 cm^2; SbS = 2.46 cm^2). Initially, the discs were subjected to a cathodic potential (−0.9 V vs. SCE) to standardize the starting conditions. Over a period of 3600 s, the open circuit potential (OCP) was monitored to evaluate the free corrosion potential of the material surface in the electrolyte solution. The electrochemical impedance spectroscopy (EIS) was used to investigate the oxide layer of cp-Ti surfaces and its properties (corrosion kinetics). Measurements of the EIS were made at a frequency of 100 kHz to 5 mHz, with AC curve in a range of ±10 mV applied to the electrode at its corrosion potential. The values were used to determine the real (Z') and imaginary (Z'') components of impedance, which were used to construct Nyquist, Bode ($|Z|$) and phase angle plots. Through EIS data, an equivalent electrical circuit was proposed to represent the electrochemical process and oxide layer properties in order to quantify the corrosion process (R_p—polarization resistance and CPE—constant phase element). The EIS data were analyzed using Echem Analyst Software