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Full Length Article

Synthesis of biofunctional coating for a TiZr alloy: Surface, electrochemical, and biological characterizations

Jairo M. Cordeiro [a,b,1], Heloisa N. Pantaroto [a,1], Emanuella M. Paschoaleto [a], Elidiane C. Rangel [c], Nilson C. da Cruz [c], Cortino Sukotjo [b,d], Valentim A.R. Barão [a,b,*]

[a] University of Campinas (UNICAMP), Piracicaba Dental School, Department of Prosthodontics and Periodontology, Av. Limeira, 901, Piracicaba, São Paulo 13414-903, Brazil
[b] Institute of Biomaterials, Tribocorrosion and Nanomedicine, Brazilian Branch (IBTN/Br), Brazil
[c] Univ. Estadual Paulista (UNESP), Engineering College, Laboratory of Technological Plasmas, Av. Três de Março, 511, Sorocaba, São Paulo 18087-180, Brazil
[d] University of Illinois at Chicago, College of Dentistry, Department of Restorative Dentistry, 801 S. Paulina, Chicago, IL 60612, USA

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ABSTRACT

This study formed a biofunctional coating for a Ti15Zr alloy to improve the surface characteristics, the electrochemical behavior, and the biological properties of this implant material. Ti15Zr discs (15 mm in diameter × 1 mm thickness) were obtained in three versions: machined, SLA®-treated (control groups), and modified by plasma electrolytic oxidation (PEO) (experimental group). Surface features such as topography, composition, surface roughness, surface free energy, and hardness were assessed. Electrochemical tests were conducted with body fluid solution (pH 7.4). The albumin protein adsorption was measured by the bicinchoninic acid method, and the adhesion of *Streptococcus sanguinis* was determined. The surface treatments modified the material's topography. SLA promoted surface roughness higher than that of the other groups, whereas PEO surfaces presented the highest values of hardness and surface free energy. PEO increased the polarization resistance and the corrosion potential, and decreased capacitance and corrosion current density values. In addition, plasma treatment improved the albumin adsorption without being favorable to biofilm adhesion. PEO appears to be the most promising alternative for Ti15Zr alloys, since it improved surface characteristics and electrochemical behavior, as well as enhancing the adsorption of albumin on the material surface with fewer tendencies to bacterial adhesion.

1. Introduction

Titanium (Ti) alloy containing zirconium (Zr) as Ti15Zr is a promising material in implantology and is used to manufacture narrow-diameter implants (< 3.5 mm), which are reliable options in rehabilitation with reduced mesiodistal and/or interradicular space or in edentulous ridges with severe reabsorption [1]. This material is commercially available as implants (Roxolid®, Institut Straumann AG, Basel, Switzerland) and has demonstrated acceptable success rates and clinical performance comparable with that of commercially pure titanium (cpTi) [2]. Its application has emerged and become established in implant dentistry due to the high levels of mechanical strength and excellent biocompatibility properties [1], and it can be considered a solution to the potential toxic effects [3] and peri-implant consequences of the Ti6Al4V alloy [4].

Adverse peri-implant effects may be caused by material degradation as a result of the release of metal ions and debris in the body. Osteolysis, bone resorption, and infections, as well as implant loosening and failure [3,5], are some negative outcomes that can occur if implant surfaces are not modified to tolerate physiological changes in the environment [6]. In addition to protecting the implant surface against corrosive and degradation processes, surface treatments can also ensure better mechanical, physical, and biological properties [7].

The surface derived by the process involving sandblasting followed by acid-etching (SLA) has demonstrated excellent clinical results when applied in implants [8], including those made by the Ti15Zr alloy. SLA implants have shown great cell differentiation and bone apposition, with strong bone-implant contact in the initial periods of osseointegration [9]. Another surface treatment that has shown promising results is plasma electrolytic oxidation (PEO),

* Corresponding author at: University of Campinas (UNICAMP), Piracicaba Dental School, Department of Prosthodontics and Periodontology, Av. Limeira, 901, Piracicaba, São Paulo, 13414-903, Brazil.
E-mail address: vbarao@unicamp.br (V.A.R. Barão).

[1] The authors share the position of first author.

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a high-voltage anodic oxidation process in electrolytic solutions [10] with good interfacial adhesion to cpTi and its alloys [11]. PEO forms rough, porous, and thick coatings [10,12], providing greater surface area for implant attachment to the bone, as well as excellent biocompatibility and osseointegration [13]. Additionally, the use of different electrolytes permits the incorporation of elements that can provide antibacterial effects [14,15], contribute to a more bioactive surface [10,16] and enhance protein adsorption [17], as well as being beneficial to the electrochemical behavior of the material [12,17].

PEO has been widely used in cpTi [12,18] and its alloys [19–21]. Moreover, to the best knowledge of the authors, it was not found studies that compared Ti15Zr alloys with PEO and SLA surfaces with regard to corrosion, protein adsorption, and biofilm formation, properties that play crucial roles in implant treatment success. Further, if Ti15Zr is to be considered a reliable material in the manufacture of dental implants, it is important that the best treatment in this bulk substrate be established. Thus, this study formed a biofunctional coating for the Ti15Zr alloy, with the aim of improving its surface characteristics, electrochemical behavior, and biological properties. For comparison with well-established surfaces, the machined and SLA surfaces were used as controls.

2. Materials and methods

2.1. Experimental design

Fig. 1 illustrates the experimental design of this study. Ti15Zr alloy discs [machined (TiZr M) and SLA® surfaces (TiZr SLA)], 15 mm in diameter and 1 mm thick, were kindly provided by Institut Straumann AG. For the experimental group, the machined surface was modified by PEO (TiZr PEO). The surface, electrochemical, and biological properties of Ti15Zr alloy were determined.

2.2. Plasma electrolytical oxidation treatment

PEO was applied according to our previous protocol [12,14,17]. Briefly, Ti15Zr machined discs were used as the anode, while a steel tank with a cooling system was the cathode. The electrolytic solution was prepared by the dissolution of 52.854 g of calcium acetate [Ca $(CH_3CO_2)_2$] (Sigma–Aldrich, St. Louis, MO, USA) and 4.3208 g of glycerophosphate disodium ($C_3H_7Na_2O_6P$) (Sigma–Aldrich) in 1 L of distilled water. The deposition was carried out in 500 mL of solution during 10 min, two discs at a time. The deposition parameters – voltage (290 V), frequency (250 Hz), and duty cycle (60%) – were controlled by a pulsed DC power supply (Plasma Technology Ltd.). The treated discs were washed with deionized water and air-dried.

2.3. Surface characterization

All samples were ultrasonically cleaned and degreased with deionized water (10 min) and 70% propanol (10 min) (Sigma–Aldrich) and dried with warm air before the characterization analyses [22]. The surface topography was observed by two- and three-dimensional images obtained by a non-contact 3D Laser Scanning Confocal Microscope (LSCM, VK-X200 series, Keyence, Osaka, Japan) (n = 1). The images were acquired with lenses of 50 × and 150 × magnification and processed by means of VK-Analyzer software (Keyence v3.3.0.0). The surface area was estimated by the extrapolation of its measurements in images of 100 × 100 μm that were obtained at the 50 × magnification. The surface morphology was also observed by means of scanning electron microscopy (SEM; JEOL JSM-6010LA, Peabody, MA, USA) (n = 1).

The main constituent elements of the Ti15Zr alloy surfaces were assessed by energy-dispersive spectroscopy (EDS) (n = 1), which allowed for semiquantitative analysis on the order of 1 μm^3. X-ray diffractometry (XRD; X'Pert PRO MRD, PANalytical, Almelo, The Netherlands) was performed to verify the chemical and microstructural composition of the surfaces (n = 1). The parameters used were: Cu–Kα (λ = 1.540598 Å) radiation and operation at 45 kV and 40 mA at a continuous speed of 0.02° per second, and a scan range from 20° to 90° [12].

Roughness parameters (average roughness, Ra; maximum height of the profile, Rt; average maximum height of the profile, Rz; and root mean square roughness, Rq) were assessed by profilometry (Dektak 150-d; Veeco, Plainview, NY, USA) with a cut-off of 0.25 mm at 0.05 mm/s over 12 s (n = 5) [23]. A goniometer (Ramé-Hart 100–00; Ramé-Hart Instrument Co., Succasunna, NJ, USA) was used to analyze the water contact angle and surface free energy by the sessile drop method (n = 5). For this test, the liquids used were water (polar component) and diiodomethane (dispersive component) (15 μL of each drop) [12]. Especially for this dependent variable, the test was performed on the TiZr M and TiZr SLA discs as soon as they were removed from the sterile package provided by the company. Therefore, the liquid's interaction with the surface could be evaluated as supplied. Vickers hardness was evaluated by means of an indenter (Shimadzu, HMV-2 Micro Hardness Tester, Shimadzu Corporation, Kyoto, Japan) (n = 5). The test was performed by the application of 0.5 kgf for 15 s at four randomly distributed points in each sample. The following formula was used to calculate the values of Vickers hardness: Hv = 1.8544

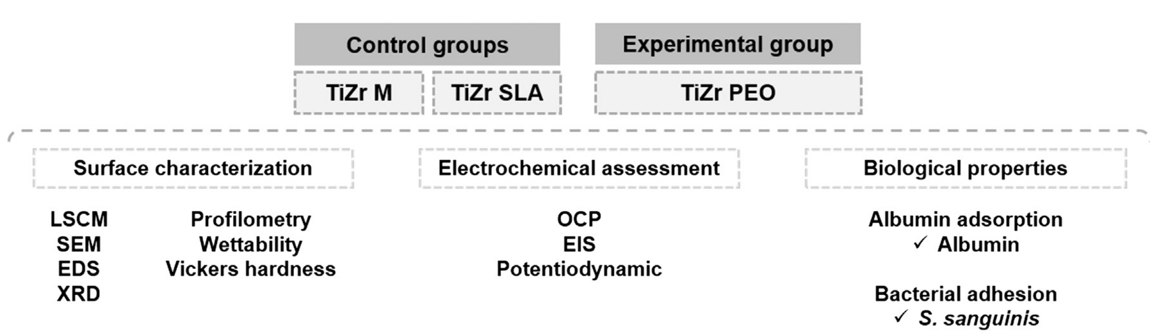

Fig. 1. Schematic diagram of the experimental design. LSCM = laser scanning confocal microscopy; SEM = scanning electron microscopy; EDS = energy-dispersive spectroscopy; XRD = X-ray diffractometry; OCP = open circuit potential; and EIS = electrochemical impedance spectroscopy.