Influence of Oxygen content on the electrochemical behavior of $Ta_{1-x}O_x$ coatings

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ABSTRACT

In this study, $Ta_{1-x}O_x$ coatings were deposited by reactive magnetron sputtering aiming at the enhancement of the electrochemical stability stainless steel 316L. The coatings were produced using variable oxygen content in order to determine its influence on the films morphological features and corrosion resistance. Structural and morphological characteristics were correlated with the corrosion behavior in artificial saliva. Potentiodynamic and electrochemical impedance spectroscopy tests were complemented with X-ray photoelectron spectroscopy to determine the electrochemical behavior of the coatings. The results reveal a more protective behavior of the coatings as the oxygen amount increases in the films, as well as pitting inhibition in the coated stainless steel, independently of the film composition. A synergetic effect between Ta_2O_5 and phosphate-based passive layers is suggested as the protective mechanisms of the coatings; while the more active electrochemical behavior of low oxygen content films is evidenced as a consequence of the metallic tantalum on the surface with a more open morphology and larger density of defects on the surface.

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1. Introduction

Nowadays, dental implants are usually fabricated using titanium (Ti) based materials due to its biocompatibility and strong corrosion resistance [1]. Ti6Al4V is the most common alloy for this application due to its higher corrosion resistance [2,3]. However, the low capacity to form a strong chemical bond with living tissue, known as bioactivity, is a significant limitation for Ti-based materials [4,5]. In fact, the number of dental implants failures associated to the healing process (osseointegration) is around 47% before artificial crown implantation and 53% during the first year of use [6]. Currently, tantalum (Ta) is proposed as an alternative to replace Ti. Ta is a bioactive element presenting interesting wettability and surface free energy which promotes osseointegration and good corrosion resistance [7–10]. The superior surface free energy of tantalum oxides stimulates the regeneration process in living tissues, and thus, increases the

efficiency of osseointegration [10–13], besides enhancing corrosion resistance due to its high chemical stability [14–16]. However, Ta presents higher prices and density comparatively with other metals [15,17]. Hence, the objective of this work is to coat stainless steel 316L (SS 316L) with $Ta_{1-x}O_x$ films to combine the enhanced bioactivity of Ta-based materials [18] with the low cost of SS 316L and evaluate the system corrosion resistance in artificial saliva.

The degradation of metallic dental implants is a common process caused by the physiological environment that surrounds the implant. Thus, additionally to an excellent osseointegration shown by the developed bioactive surfaces, it is mandatory to further evaluate their corrosion properties in order to obtain an appropriate coating performance.

Previous works studying the corrosion of Ti-based dental implant materials reported that the stability of the TiO_2 protective passive layer (Me-O) is pH dependent and can degrade in the oral environment due to the presence of corrosive substances on saliva [19,20]. As mentioned before, Ta-based materials can replace Ti dental implants. Consequently, it is important to note that only few studies report the corrosion performance of Ta-based materials and are out of the scope of dental implant application. Mostly, the studies focus on Ta corrosion behavior influenced by crystalline phases [21,22] or surface roughness [23] in acid environments (*i.e.* H_2SO_4), or on the influence of different Ta deposition methods on

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the corrosion performance in saline environments (NaCl), testing steel corrosion protection approaches [24]. For instance, it has been reported that coatings with α-Ta or β-Ta phases showed protective behavior to steel substrates being dependent on the presence of defects such as pinholes or porosity. The corrosion processes is controlled by the steel dissolution through the open pores. Still, β-Ta structure is more susceptible to suffer corrosion due to its brittle nature [21,22]. Additionally, it was found that the corrosion protection was maintained even using substrates with different roughness [23]. On the other hands, the electrochemical performance for tantalum oxides has shown to be dependent on the oxide morphology/density, revealing a lower coating break-down potential and faster pit growth in highly porous Ta_2O_5. Furthermore, some studies are focused on Ta_2O_5 corrosion performance for bio-applications, due to the high biocompatibility and bioactivity, however in Simulated Body Fluid (SBF) environment [16,25], which present a more neutral character compared to simulated saliva. Besides the improvement of corrosion resistance of Ti by Ta-based coating, denser Ta_2O_5 coating improves corrosion resistance in biological environments [16,25].

As a result, this work is focused on the electrochemical assessment in artificial saliva of Ta and tantalum oxide films produced by DC reactive magnetron sputtering and the determination of the structural and morphological effect on the electrochemical characteristics.

2. Experimental Details

2.1. Coatings deposition

Ta-based films were deposited onto polished stainless steel 316L (SS 316L) ($20 \times 20 \, mm^2$) and single crystalline silicon (100) ($1 \times 1 \, mm^2$) substrates by reactive DC magnetron sputtering using a high-purity Ta target (99.6% Ta) ($200 \times 100 \, mm^2$). The SS 316L substrates were grinded using emery paper from 600 to 2400 grit and then mirror polished with a diamond solution, attaining a surface roughness <3 nm. All the substrates were ultrasonically cleaned using distilled water, ethanol and acetone for 10 min in each solvent.

The substrates were located at 70 mm in front of the target and the rotation speed and deposition temperature were kept constant at 7 rpm and ~200 °C, respectively. Previous to each deposition, the substrates were sputter-etched to remove remaining impurities and surface oxides on the target and substrate surface, improving film adhesion. To further enhance the coatings adhesion a Ta interlayer was deposited, with approximately 200 nm. The interlayer deposition was carried out with a current density of $10 \, mA \, cm^{-2}$ in Ar atmosphere (0.6 Pa) at constant bias voltage (−75 V). The film depositions were carried out in Ar+O_2 atmosphere with a constant bias voltage of −75 V. The current density applied to the Ta target was varied from 10 to 5 mA cm^{-2} in order to achieve stoichiometric tantalum oxide. Ar flow was kept constant while the O_2 flow was adjusted, as depicted in Table 1. The base

pressure was 6×10^{-4} Pa and the discharge pressure ranged from 0.6 to 0.7 Pa depending on the gas flow.

2.2. Coatings characterization

The coating chemical composition was determined by Cameca SX50 electron probe microanalysis (EPMA) equipment, operating at 10 kV and 40 nA. Scanning electron microscopy (SEM) was used to observe the surface and cross-sectional morphology of the films and measure the film thickness employing a NanoSEM – FEI Nova 200 (SEM) operating at 5 keV and a LEICA S360 microscope, operating at 15 kV in secondary electron mode. XPS analysis was performed using a Kratos AXIS Ultra HSA, with VISION software for data acquisition and CASAXPS software for data analysis. The analysis was carried out with a monochromatic Al Kα X-ray source (1486.7 eV), operating at 15 kV (150 W), in FAT mode (Fixed Analyser Transmission), with a pass energy of 40 eV for regions ROI and 80 eV for survey. Data acquisition was performed with a pressure lower than 1×10^{-6} Pa, and a charge neutralisation system was used. The effect of the electric charge was corrected by the reference of the carbon peak (285 eV).

Optical micrographs were obtained to analyze the size, area and distribution of surface defects using ImageJ software and a subsequently descriptive statistical analysis was performed. EPMA, SEM and XRD analysis were performed in coatings deposited onto Si substrates, while XPS analysis and optical microscopy were performed on coatings deposited onto SS 316L.

2.3. Electrochemical experiments

The corrosion performance was assessed by open circuit potential (OCP), electrochemical impedance spectroscopy (EIS) and anodic potentiodynamic polarization experiments. The apparatus for electrochemical measurement consisted of a Gamry REF600 potenciostat controlled by EIS300 and DC105 software. Electrochemical experiments were carried out with a standard three-electrode cell. A saturated calomel electrode (SCE) was used as the reference electrode with a platinum counter electrode and the SS 316L coated with Ta-based film as the working electrode, with an exposed area of 0.44 cm^2. The experiments were performed on CP Ti grade 2 (Gr2) (ASTM: F67) as a commercial surface control, on SS 316L as surface control and on $Ta_{1-x}O_x$ coatings as a developed surfaces. Each sample was immersed into a volume of 200 ml of Fusayama artificial saliva (0.4 wt.% NaCl; 0.4 wt.% KCl; 0.795 wt.% $CaCl_2 \cdot 2H_2O$; 0.005 wt.% $Na_2S \cdot 9H_2O$; 0.69 wt.% $NaH_2PO_4 \cdot 2H_2O$; and 1 wt.% Urea) with stabilized pH at 5.5 in equilibrium with air. The tests were performed at room temperature, under static conditions. Three measurements were performed for each sample to statistically validate the results. OCP and EIS experiments were carried out as a function of the immersion time after 2, 24 hours and 7 days. Before each impedance experiment, a stable OCP potential was achieved during 1 hour for the first measurement and 30 min for the

Table 1
Chemical composition, deposition parameters, thickness and deposition rate of the deposited samples.

Sample	Chemical composition (at.%)		O_2 Flow (sccm)	Currenty density (mA cm^{-2})	Thickness (μm)	Deposition rate (μm h^{-1})
	Ta	O				
TO6	95 ± 0.3	5 ± 0.3	0	10	4.5	2.3
TO1	89 ± 0.6	11 ± 0.6	2	10	4.2	2.1
TO5	57 ± 0.2	43 ± 0.2	10	10	5.5	2.8
TO6	30 ± 0.4	70 ± 0.4	13	5	3.8	1.9