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Growth and Electrochemical Stability of Compact Tantalum Oxides Obtained in Different Electrolytes for Biomedical Applications

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Tantalum has been cited to have many biomaterial applications, exhibiting biocompatibility and outstanding corrosion resistance. Tantalum may be covered with tantalum oxide using the electrochemical process of anodic oxidation. The oxide surface is known to be bioactive and more corrosion resistant. In this research, compact tantalum oxide films were obtained by potentiostatic and potentiodynamic methods in H_2SO_4 and H_3PO_4 (1 mol.L^{-1}) electrolytes. By XPS analysis the stoichiometry Ta_2O_5 was detected. The thermodynamic stability of those oxides was compared and the results indicated that Ta_2O_5 obtained in H_2SO_4 has higher thermodynamic stability than Ta_2O_5 obtained in H_3PO_4. The incorporation of $(PO_4)^{3-}$ ions and the formation of a bilayer oxide are responsible for the reduced stability. Also, the better control of chemical kinetic of oxide formation allows potentiodynamic oxides to be more stable. Ta_2O_5 shows spontaneous dissolution in artificial blood, nevertheless, it remains stable even after 60 days of immersion. By scratching tests was possible to notice that Ta_2O_5 is highly adherent to the tantalum metallic substrate and by mechanical indentation was possible to measure a lower elastic modulus for the Ta_2O_5 than the metallic substrate, what can be considered as distinguished properties for biomedical applications.

Keywords: *biomaterial, tantalum, anodic oxide, electrochemical stability*

1. Introduction

Metals used in biomedical appliances must show particular properties, depending on its specific utilization. The main property to be considered is biocompatibility, followed by corrosion resistance and mechanical properties. For being highly resistant to corrosion in corporeal media, metallic titanium and its alloys have been mostly used[1]. Concerning biomaterials, researches regarding tantalum are motivated by its great corrosion resistance[2]. Nowadays, many researchers[3-5] are studying Ti-Ta alloys since its lower density, lower cost and superior corrosion resistance, as compared to titanium, makes them extremely promising. Although tantalum can be used in its metallic form, the natural oxide (Ta_2O_5) may improve its bioactive response and chemical attack resistance[6]. The electrochemical method of anodic oxidation is one the most versatile process towards the growth of oxides on valve metals like tantalum and titanium[7]. Some authors[8,9] have already studied the influence of the anodization parameters in anodic oxides properties. About Ti-Zr alloys, higher stability oxides were obtained when higher potentials were applied[8]. Also, higher or lower thermodynamical stabilities were achieved in different acidic electrolytes[8]. On titanium surfaces, thicker oxides were obtained in higher polarization potentials[9].

The mechanism and kinetics of Ta_2O_5 formation in aqueous solutions were discussed by many researches[10-14], and most of these studies consider the oxide formation in dilute acidic electrolytes of H_2SO_4 and H_3PO_4. In these acids, Ta_2O_5 may incorporate electrolyte anions as $(SO_4)^{2-}$ or $(PO_4)^{3-}$ to its structure besides of O^{2-}, wherein the phosphate ion are the most likely to be incorporated[10,12]. Several properties of tantalum oxide may be modified by the incorporation of electrolyte anions, mainly its chemical stability and the formation of a bilayer oxide[12,13].

This research had the purpose to compare the thermodynamic stability of tantalum oxides grown by different anodization methods and potentials in dilute H_2SO_4 and H_3PO_4, as well as the spontaneous dissolution resistance in artificial blood media by open-circuit potential (OCP) method. This research also evaluated mechanical properties, as elastic modulus and scratching resistance, for the grown oxide.

2. Experimental

Samples of tantalum (99.9%+) measuring 1 mm thick, 2 cm² were provided by Sigma-Aldrich Brasil Ltda. For surface preparation, the samples were grounded up to grid 600 sandpaper and then sonicated in three sequential baths: pure acetone, isopropyl alcohol and distilled water (15 minutes each).

The anodization processes were made in a conventional three electrode electrochemical cell. The working electrode was pure tantalum with 0.28 cm² of exposed area to the

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electrolyte. A spiral platinum wire was used as counter electrode and all potentials were measured against a saturated calomel electrode (SCE). Working and counter electrode were connected to a Power Supply (Minipa – MPL 1305M) for potentiostatic oxidation at stationary potentials of 5 V and 20 V during 1 h. For potentiodynamic oxidation a potential sweep between -1.0 and 5.0 V (50 mV/s) was used in a potentiostat-galvanostat (Microquímica - MQPG-01). Two acidic electrolytes were used: H_2SO_4 (1 mol.L^{-1}) and H_3PO_4 (1 mol.L^{-1}). All oxidation experiments were performed at room temperature. To characterize the surface oxide, XPS (X-ray Photoelectron Spectroscopy) analysis were performed using a VG Microtech ESCA3000 spectrometer having an A1Kα X-Ray source in 3.10^{-8} Pa pressure and 20 eV energy band.

To compare the electrochemical stability of the new oxidized surfaces, OCP (Open Circuit Potential) of all surfaces was measured. Also, the dissolution process of oxidized surfaces was studied before and after immersion in artificial blood by different periods at 37 °C. The stabilization time of OCP potentials was fixed in 90 minutes. These potentials were measured in PBS (Phosphate Buffer Solution) media that contains NaCl 8.0 g.L^{-1}, KCl, 0.2 g.L^{-1}, Na_2HPO_4 1.15 g.L^{-1} and KH_2PO_4 0.2 g.L^{-1}, commonly used solution in electrochemical tests. Samples were exposed to artificial blood (at 37 °C) during 15, 30 and 60 days. Artificial blood is composed of NaCl 6.80 g.L^{-1}, KCl 0.40 g.L^{-1}, $CaCl_2.H_2O$ 0.20 g.L^{-1}, $NaH_2PO_4.H_2O$ 0.02 g.L^{-1}, $Na_2HPO_4.H_2O$ 0.126 g.L^{-1}, $MgSO_4$ 0.10 g.L^{-1}, $NaHCO_3$ 2.20 g.L^{-1} (pH ~ 7.45). PBS and artificial blood solutions have their chemical composition described in ASTM – F2129-08.

To evaluate the mechanical properties (elastic modulus and adherence to substrate) a MTS instruments – Nano Indenter XP was used. Instrumented indentation measures were made with a Berkovich tip with a maximum load of 1 gf with eight complete cycles of loading and unloading in a matrix of 25 sites. The mechanical properties were collected from analyses of load-displacement data using the Oliver-Pharr method[14]. The scratching tests were made using a Berkovich tip and three maximum loads: 10, 30 and 50 mN with three scratches in each load. Scratches were made in ramp with a constant displacement speed of 10 µm/s along 600 µm, it was used scanning electron microscopy to analyze the scratches.

3. Results and Discussion

By anodic oxidation, compact tantalum oxides were obtained on the working electrodes. All the chronoamperometric profiles (Figure 1) showed the typical behavior of valve

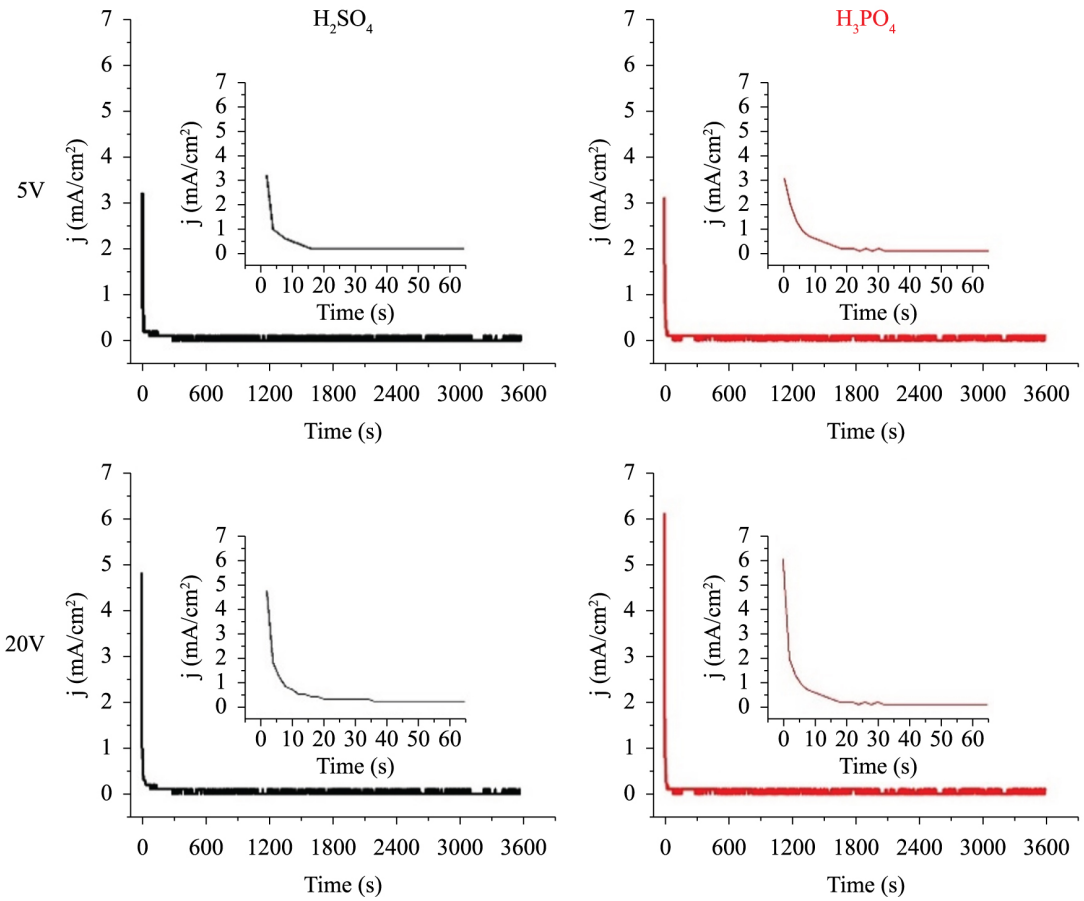

Figure 1. Chronoamperometric profiles for tantalum oxides obtaining at 5 V and 20 V in H_2SO_4 and H_3PO_4 (1 mol.L^{-1}). Insets represents the first seconds of the process.

metals, with a maximum of current density in the very beginning of the process, associated to the fast formation of an insulating oxide. As the process is continued, the current density undergoes a sudden decay due to the oxide insulating behavior and reaches a stable plateau of mA or even μA, where reactions of oxidation and reduction still occurs in slower kinetics, since migration of ions is needed to the thickening of the oxide layer. The anodization was the only process noticed. As all chronoamperometric profiles of Figure 1 are very similar, it's assumable that the kinetics of formation of the potentiostatic tantalum oxide is mainly influenced by the method of anodization and the applied potential, whereas different electrolytes, containing $(PO_4)^{3-}$ or $(SO_4)^{2-}$ ions, seems to have similar chemical kinetics. The potential sweep for potentiodynamic method for both electrolytes is also very similar (Figure 2 and Figure 3), showing a sudden inversion of current density from cathodic to anodic, with a current density peak in approximately 0.25 V for H_2SO_4 and 0.02 V for H_3PO_4, and a plateau until 5 V for both electrolytes. The displacement between peaks may be related to the greater oxidant behavior of H_3PO_4 due to its higher dissociation in aqueous media. Those behaviors indicate the formation of an oxide that features high electrical resistance.

XPS analysis of the oxidized samples indicated the Ta_2O_5 stoichiometry as the superficial oxide, independently of the electrolyte. Both samples presented peaks referring to tantalum and oxygen bonded to each other in the stoichiometry Ta_2O_5[15,16] (Figure 4 and Figure 5). Tantalum in $Ta/Ta_2O_5 - H_2SO_4$ was detected by a doublet in approximately 26 eV and oxygen by a singlet in approximately 530 eV. Similarly, $Ta/Ta_2O_5 - H_3PO_4$ presented a doublet associated to tantalum in approximately 26 eV and a singlet to oxygen in approximately 530 eV. The sample oxidized in H_3PO_4 exhibited also a peak in approximately 133 eV associated to phosphorus bonded to oxygen, indicating that a mixed oxide of tantalum and phosphorus may be formed[17,18] (Figure 5). This result indicates that electrolyte anions, mainly phosphates, are indeed incorporated to the forming oxide during anodization.

In order to compare the electrochemical stability of the tantalum oxides obtained by different electrochemical methods, electrolytes and potentials, OCP tests were made and the results are shown in Table 1. Oxide growth methods differ on its electrochemical parameters control, mainly the chemical kinetics of oxide formation[19]. The uniform formation kinetic

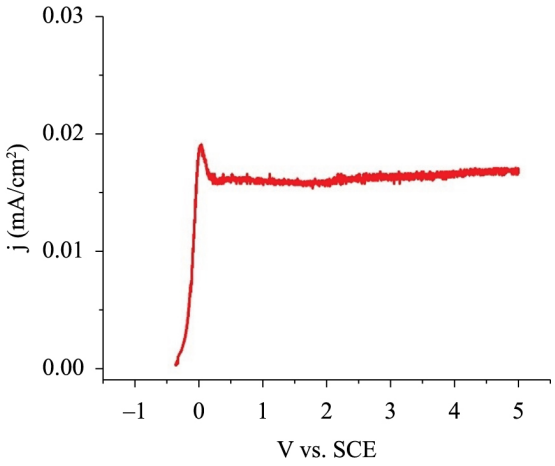

Figure 2. Potential sweep profile for tantalum oxide obtained up to 5 V (50 mV/s) in H_2SO_4 (1 mol.L^{-1}).

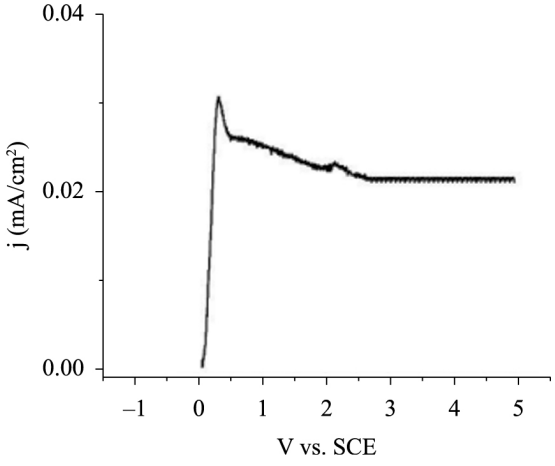

Figure 3. Potential sweep profile for tantalum oxide obtained up to 5 V (50 mV/s) in H_3PO_4 (1 mol.L^{-1}).

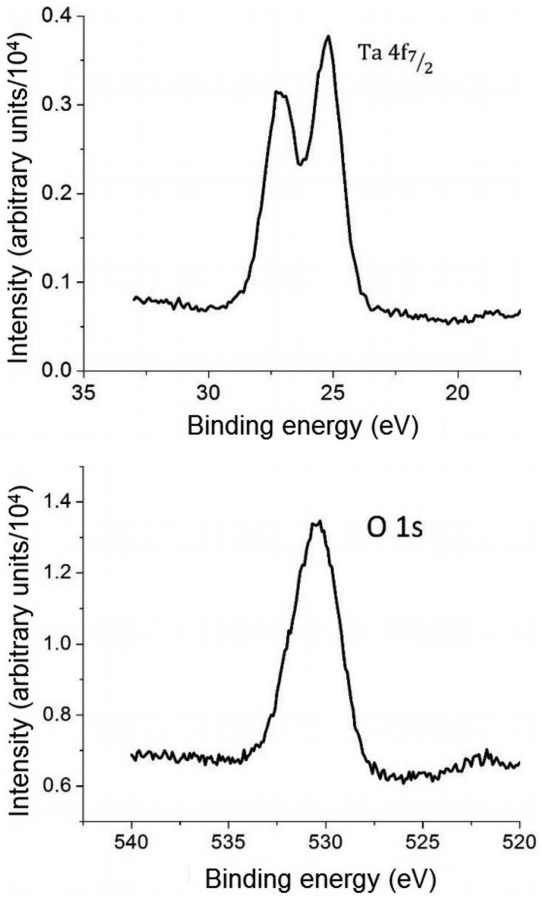

Figure 4. XPS spectra for tantalum and oxygen of the sample of tantalum oxide obtained in H_2SO_4.

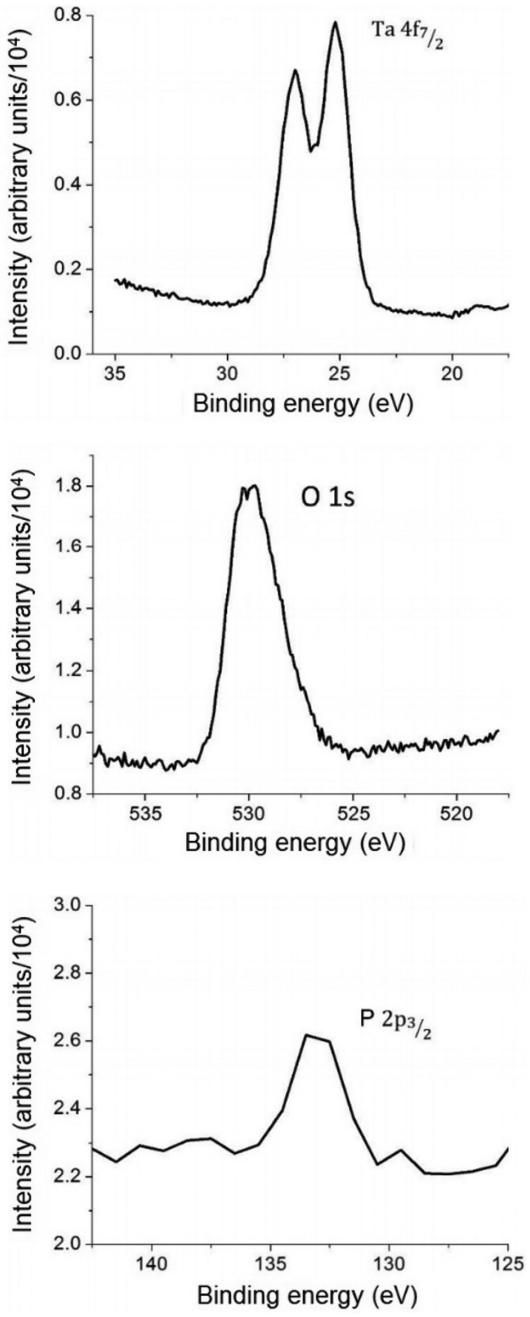

Figure 5. XPS spectra for tantalum, oxygen and phosphorus of the sample of tantalum oxide obtained in H_3PO_4.

Table 1. OCP values for tantalum oxides grown by potentiostatic and potentiodynamic methods in H_2SO_4 and H_3PO_4 (1 mol.L^{-1}).

Method	OCP / mV (vs. SCE)	
	H_3PO_4 (1 mol.L^{-1})	H_2SO_4 (1 mol.L^{-1})
Potentiostatic 20 V (1 h)	-17.3	-5.42
Potentiostatic 5 V (1 h)	-67.2	-42.3
Potentiodynamic Ei = -1.0 V, Ef = 5.0 V	-38.4	-22.8

during the potential sweep in potentiodynamic conditions possibly allows the formation of a highly ordered and more stable oxides[19]. The higher stability of potentiodynamic oxides may be observed in Table 1. Surfaces obtained potentiodinamically presented OCP at -38.4 mV (H_3PO_4) and -22.8 mV (H_2SO_4) whereas potentiostatic oxides showed OCP at -67.2 mV (H_3PO_4) and -42.3 mV (H_2SO_4). Although the potential was applied for one hour in potentiostatic condition, the results indicated that time have no effect on the measured equilibrium potential. Thus, the anodic oxide growth on tantalum surfaces follows the High Field Model and its growth rate is mainly function of the applied potential and constants that are typical to every oxide[20]. As described in Marino's research[20] with anodic charges of the Ti-oxide growth, the anodization rate was determined by electrochemical methods and was found to be 2.5 nm/V.

Regarding the thermodynamic stability of the oxides grown potentiostatically at 5 V and 20 V, Table 1 presents OCP at -67.2 mV (H_3PO_4) and -42.3 mV (H_2SO_4) for oxides grown at 5 V and -17.3 mV (H_3PO_4) and -5.42 mV (H_2SO_4) for oxides grown at 20 V. The higher stability of oxides grown at 20 V may be associated to its larger thickness (20 nm for 5 V and 77 nm for 20 V). A thicker oxide may have a higher resistive behavior[21].

The thermodynamical stability of oxides grown in different acidic electrolytes may be compared. Independently of the electrochemical method or applied potential, oxides grown in H_2SO_4 shown more positive equilibrium potential and consequently, higher thermodynamical stability. As described by several researches[10,13], the oxides grown in dilute H_2SO_4 are homogeneous and shown least amounts of $(SO_4)^{2-}$ incorporation on its structure. Tantalum oxides grown, even in dilute, H_3PO_4 electrolytes shown considerable amounts of $(PO_4)^{3-}$ incorporated to the oxide, enabling the formation of less stable dual layer mixed oxide[10-13].

By the OCP data (Table 2) was possible to study the dissolution process of tantalum anodic oxides in aggressive fluid media. The tantalum oxide layer presented more positive equilibrium potential values, compared to pure tantalum, independently of the acid electrolyte. It indicates that the oxidized surfaces are more stable due to the oxide presence. When the immersion time of the oxides was 15 days, the equilibrium potential becomes more negative around -34.7 mV (sulphate media) and -65.4 mV (phosphate media). The same tendency occurs with Ta/Ta_2O_5 (20 V-1 h) in artificial blood, as -73.2 and -109 mV after 60 days. The oxidized surface remains stable even after 60 days considering that pure tantalum has the lowest stability with an OCP of -660 mV. This result indicates that Ta_2O_5 is a highly stable oxide, resistant to dissolution/corrosion process in a simulated corporal aggressive media. Tantalum oxides obtained in sulphate media presented a higher thermodynamical stability and this tendency was kept during the whole experiment time.

The tantalum oxide grown in H_3PO_4 (1 mol.L^{-1}) may present a dual layer structure[7], which may contribute to its lower stability[8]. Many authors described[10-13] that the phosphate ions could be incorporated to the tantalum oxide structure and consequently a mixed oxide of tantalum and phosphorus are formed. This result agrees to the XPS spectra of the samples of Ta_2O_5 obtained in H_3PO_4 of this research, indicating that

Table 2. OCP values for bare tantalum and its oxides obtained in H_2SO_4 and H_3PO_4 (1 mol.L^{-1}) before and after immersion in artificial blood by 15, 30 and 60 days.

Immersion time in artificial blood at 37 °C (days)	OCP / mV (vs. SCE)		
	Bare Tantalum	Ta_2O_5 / H_2SO_4 (1 mol.L^{-1})	Ta_2O_5 / H_3PO_4 (1 mol.L^{-1})
0	-660	-5.42	-17.3
15		-34.7	-65.4
30		-52.8	-96.5
60		-73.2	-109

possibly has incorporated phosphorus species. Mixed oxides has variable structure and chemical composition along its thickness, with a compact inner layer composed mainly of stoichiometric Ta_2O_5 and a porous outer layer composed of Ta_2O_5 and incorporated phosphates[10-13]. Those incorporated phosphates may be interpreted as point defects of chemical inhomogeneity that increases its chemical reactivity and its susceptibility to dissolution/corrosion in aggressive media[11]. Researchers[12] studied the dissolution resistance of tantalum oxide layers in aggressive media (F^- ions) and also noticed that the dissolution rate of mixed oxides is superior if compared to stoichiometric Ta_2O_5. Possibly, the outer layer of the oxide grown in H_3PO_4 (1 mol.L^{-1}) provides a higher reactivity in aggressive media and it may be detected by its more negative equilibrium potential value.

Lower elastic modulus is preferable for metallic biomaterials since it helps to avoid phenomenon of stress shielding. It happens when the implant supports most of the loads, since it has a higher elastic modulus when compared to the human bone (~30 GPa), leaving the bone underused. Stress shielding may lead to bone reabsorption, loosening of the implant or even another bone fracture[22]. A lower elastic modulus material supports a uniform distribution of load between implant and bone[23]. Pure tantalum elastic modulus is about 186 GPa, which is higher than the 110 GPa of pure titanium, but yet lower than 220 GPa and 190 GPa of cobalt-chrome alloys and some stainless steels used for implants, respectively. By the instrumented indentation tests, the elastic modulus of the tantalum oxides obtained potentiostatically in H_2SO_4 e H_3PO_4 was measured Firstly, it was analyzed the Ta_2O_5 film obtained in sulfate ions containing media. The analysis of Figure 6 allows us to assume that there is a relation between the depth of contact and the elastic modulus, indicating that the obtained oxide should be homogeneous. Higher loads resulted in deeper penetrations and therefore a greater influence of the substrate in the measure. As there is a considerable influence of the substrate even in the first measure, in about 30 nm, it cannot be affirmed that the elastic modulus of the film is equal to the first indentation, however, it can certainly be stated that the elastic modulus is lower than 186 GPa of the substrate. With increasing loads and deeper penetrations, the measured elastic modulus increases due to the higher contribution of the substrate in the measure, approaching asymptotically to values close to the substrate. Tests in tantalum oxide obtained in phosphate medium showed reduced elastic modulus, of the order of 125 GPa at the first indentations, indicating that this material has a lower elastic modulus compared to the substrate. The incorporation of electrolyte species to the outermost layer of the oxide promotes the formation

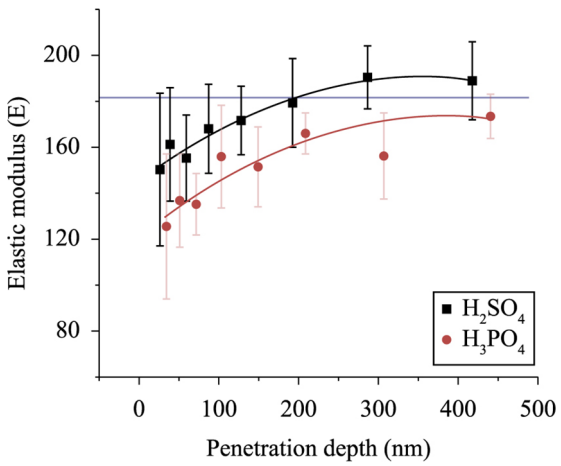

Figure 6. Elastic modulus as function of the penetration depth with a Berkovich tip in tantalum oxides obtained potentiostatically 20 V (1 h) in H_2SO_4 and H_3PO_4 (1 mol.L^{-1}). The straight line represents the metallic tantalum elastic modulus (186 GPa).

of a mixed oxide of tantalum and phosphorus. This bilayer oxide apparently has a lower elastic modulus because it was less compact. Summarizing, the acidic electrolyte used for potentiostatic tantalum anodizing influences the mechanical properties of Ta_2O_5 obtained anodically. The formation of a bilayer tantalum oxide (in H_3PO_4 1 mol.L^{-1}), which may vary in chemical composition and densification along its thickness, can promote a lower elastic modulus on its outer layer. An oxide of uniform composition and dense throughout its thickness, as the oxide obtained in H_2SO_4 (1 mol.L^{-1}), tends to have a higher elastic modulus, even in small penetrations. It cannot be stated precisely the elastic modulus of the oxide, since the contribution of the substrate measured, however, it can be confirmed that tantalum oxides obtained in both acidic electrolytes have lower elastic modulus than the substrate and therefore anodization can be considered a good surface treatment for bone apposition.

Scratching tests were carried out to end loads of 10, 30 and 50 mN, however, only the scratches with load of 50 mN were observed. Although the scratches undertaken to 50 mN were noticeable, there was no tearing of the surface oxide, indicating that the anodic oxides obtained in the employed electrochemical conditions are strongly adherent to the metal substrate of tantalum. The micrograph of the scratch performed on the Ta_2O_5 anodic film obtained potentiostatically in H_3PO_4 (1 mol.L^{-1}) is presented in Figure 7. The original topographic profile and the residual scratch of the sample (after scratching) are presented in Figure 8. These profiles

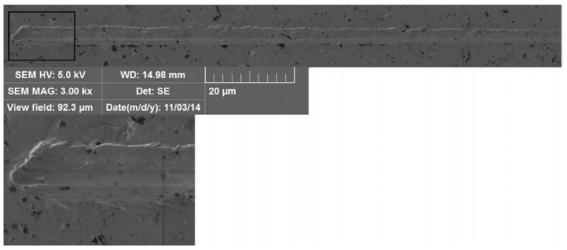

Figure 7. SEM of the 50 mN scratch on the 20 V (1 h) H_3PO_4 (1 mol.L^{-1}). Image obtained with a magnification of 3000x.

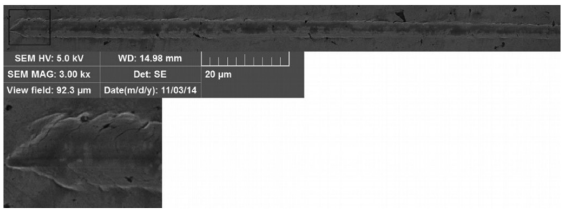

Figure 9. SEM of the 50 mN scratch on the 20 V (1 h) H_2SO_4 (1 mol.L^{-1}). Image obtained with a magnification of 3000x.

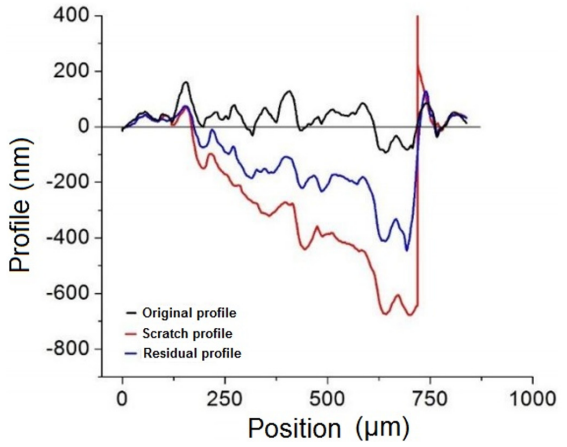

Figure 8. Original, scratch and residual profiles of the 20 V (1 h) H_3PO_4 (1 mol.L^{-1}) tantalum oxide.

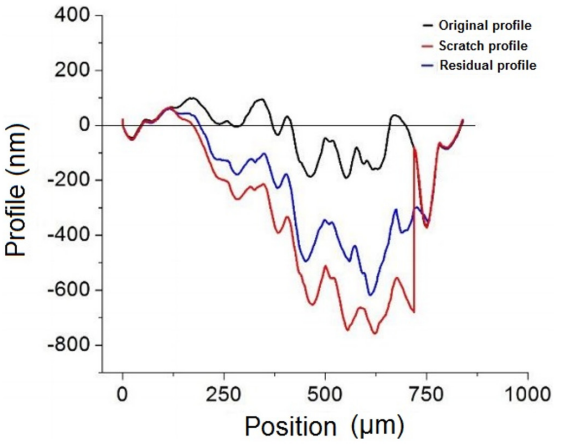

Figure 10. Original, scratch and residual profiles of the 20 V (1 h) H_2SO_4 (1 mol.L^{-1}) tantalum oxide.

were obtained using a profilometer of the equipment used for scratching. For topographic profiles and the profile analysis after scratch (residual profile), it can be seen that the Ta/Ta_2O_5 material possess great capacity for deformation without fracture, i.e, the material is plastically deformed but also elastically returns to a state of low strain.

The scratch performed in the tantalum oxide obtained in H_2SO_4, (Figure 9) similarly to the scratch showed in tantalum oxide obtained in H_3PO_4, does not indicate tearing of the film to the maximum load of 50 mN. Again, the oxide was highly adherent to the substrate, with capacity of deformation without fracture. In both cases (Figure 8 and Figure 10), the residual profile is an intermediate profile between the original profile and the scratch profile, once again indicating that the tantalum oxide in the form of thin film (~77 nm) has high deformation capacity without fracture, i.e, the material has residual plastic deformation but elastically returns to a closer form to the original. In addition, by the profiles can be seen that the load used was heavy enough so that the substrate was also deformed.

The analysis of microscopy with the topographic profile, allows to compare these results to studies already described in the literature[24,25]. Eliezer & Brandon[24] apud Bubar & Vermilyea[25] observed plastic deformation around 50% for galvanostatic anodic films of Ta_2O_5 obtained in acidic electrolytes, which indicates a highly adherent oxide for this feature in the proposed dimensions (thin film). In another research, Dunn[26] observed through lamination that tantalum samples with Ta_2O_5 films grown galvanostatically in acidic electrolytes had high deformation capacity. The researcher also noted that the thickness of the tantalum oxide decreases evenly throughout the specimen, without fracture and without the detachment of the film, indicating that this material support plastic deformation[26,27]. Analyzing the images from SEM in Figures 7 and 9 once again, it is noted that the scratches on samples of tantalum oxide obtained in both acidic electrolytes are very similar. It is possible that higher porosities content in the outer layer of a tantalum bilayer oxide obtained in phosphate media could make deformation of the film less uniform and more subject to fractures, however, this behavior could not be observed by the SEM images. It is possible that the small thickness of the oxide layer (~77 nm) has precluded this analysis.

4. Conclusions

The electrochemical growth of compact tantalum oxides by different electrochemical methods, potentials and acidic electrolytes is possible and reproducible. Phosphate ions from the electrolyte were possibly incorporated and a mixed tantalum/phosphorus oxide was formed. Besides, a bilayer oxide may be grown in phosphate media, with a compact inner layer and a reactive and porous outer layer. The greater chemical reactivity of the outer layer could facilitate the spontaneous dissolution rate of tantalum oxide in aggressive media as artificial blood. The tantalum oxides grown in sulphate media, in higher potentials and by potentiodynamic electrochemical method presented higher thermodinamical

stability due to its chemical homogeneity, higher thickness and structural organization, respectively. Regarding the mechanical properties: the tested tantalum oxides presented lower elastic modulus than metallic tantalum (186 GPa). This result indicates that the tantalum oxide might be a more suitable substrate for bone-implant contact. Tantalum oxides obtained in $(PO_4)^{3-}$ media presented lower elastic modulus, which confirms the possibility of the formation of a more porous oxide in the outer layer of this oxide. Bilayer oxides may influence mechanical properties of tantalum anodic films. The scratching tests showed that all anodic films are highly adherent to the metallic surface, not being pulled of even in higher loads (50 mN). The obtained results indicates that the system Ta/Ta_2O_5 is a stable material, presenting high chemical inertia in body simulated corrosive media, high adherence to the metallic substrate and a lower elastic modulus than the metallic tantalum, indicating that it might be applied as a biomaterial.

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