Bioactivity response of Ta$_{1-x}$O$_x$ coatings deposited by reactive DC magnetron sputtering

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The use of dental implants is sometimes accompanied by failure due to periimplantitis disease and subsequently poor esthetics when soft–hard tissue margin recedes. As a consequence, further research is needed for developing new bioactive surfaces able to enhance the osseous growth. Tantalum (Ta) is a promising material for dental implants since, comparing with titanium (Ti), it is bioactive and has an interesting chemistry which promotes the osseointegration. Another promising approach for implantology is the development of implants with oxidized surfaces since bone progenitor cells interact with the oxide layer forming a diffusion zone due to its ability to bind with calcium which promotes a stronger bond.

In the present report Ta-based coatings were deposited by reactive DC magnetron sputtering onto Ti CP substrates in an Ar + O2 atmosphere. In order to assess the osteoconductive response of the studied materials, contact angle and in vitro tests of the samples immersed in Simulated Body Fluid (SBF) were performed. Structural results showed that oxide phases where achieved with larger amounts of oxygen (70 at.% O). More compact and smooth coatings were deposited by increasing the oxygen content. The as-deposited Ta coating presented the most hydrophobic character (100°); with increasing oxygen amount contact angles progressively diminished, down to the lowest measured value, 63°. The higher wettability is also accompanied by an increase on the surface energy. Bioactivity tests demonstrated that highest O-content coating, in good agreement with wettability and surface energy values, showed an increased affinity for apatite adhesion, with higher Ca/P ratio formation, when compared to the bare Ti substrates.

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1. Introduction

Several materials have been proposed for use as dental implants, namely, 316L stainless steel (SS 316L) [1], chromium–cobalt–molybdenum alloy (Cr-Co-Mo) [2], hydroxyapatite (HAp) [3], zirconia (ZrO$_2$) and/or alumina (Al$_2$O$_3$) [4] but only a few of them have been accepted such as commercially pure titanium grade 2 (CP Ti Gr2) [5,6] and titanium–aluminium–vanadium alloy (Ti6Al4V–Ti Gr5) [7–10]. Currently, most dental implants are manufactured on CP Ti Gr2 or Ti Gr5, with threaded geometries with internal connections for the abutments [11]. Nowadays, conventional implants can be manufactured with a porous microstructure propitiating a more efficient bone tissue ingrowth by the increase of the specific surface in contact with the surrounding media [5]. Nevertheless, commercial dental implants still present a number of limitations and their use is sometimes accompanied by failure [12,13]. The slow osseointegration of Ti dental implants leads to slow loading of the implant by the artificial crown, thus requiring a long non-operational time [12,14], which enhances the probability of microorganisms entrance on the oral environment close to the surgical site, specifically to the surface of the dental implant. The adhesion and possible microbial colonization can induce the appearance of infections with consequent post-surgical complications [15,16]. Infections are the main responsible for the short, medium and long-term failure of the dental implants. Failure due to periimplantitis disease, which is the most common, is related with the late infection of the adjacent bone tissue that makes the bone recede and subsequently a decrease in the mechanical anchorage of the implant is observed. As a consequence, when the soft–hard tissue recedes, the “gray” Ti is exposed with a consequent poor esthetics [17,18]. These limitations are mainly associated with the poor bioactivity of Ti (ability to stimulate the formation of new apatite containing tissue) [19]. For achieving the integration of the implant with the surrounding bone tissue, further research is needed for developing new highly bioactive surfaces able to enhance and promote the osseous growth and bone matrix mineralization.

In the last years, there has been a great interest in the modification of surface characteristics of dental implants as a demand for bioactive surfaces that enhance the implant healing process [20]. In our days tantalum (Ta) is pointed as a promising material since, comparing to Ti, it is bioactive and has interesting chemistry valences which promote a
higher biomineralization kinetics enhancing the osseointegration [13, 21–25]. According to Balla et al. [26] a layer of hydroxyapatite was rapidly formed on a Ta surface immersed in simulated body fluid (SBF), revealing a strong chemical bond due to the high surface energy of Ta, compared to CP Ti. In addition, Frandsen et al. [27] found that Ta shows a better biological behavior compared to titanium dioxide (TiO2) surfaces, when alkaline phosphatase activity tests were performed. In fact, Ta revealed a faster rate of matrix mineralization (≈30%) due to its surface chemistry properties.

The major drawback of Ta is its high cost, which makes Ta dental implants less cost effective [28]. However, since the bioactivity is determined by surface properties [29], the surface modification of the implants with Ta coatings represents a challenging selection for the development of bioactive surfaces.

Another promising approach for implantology is the development of implants with oxidized surfaces [30,31]. In fact, bone progenitor cells interact with the oxide layer forming a diffusion zone due to its ability to bind with calcium which promotes a stronger bond [23,24,32], besides enhancing the corrosion resistance [25,33]. Then, the surface modification of Ti implants with tantalum oxide coatings can also play an important role in the interface between the bone and the implant.

The aim of this work is the development of bioactive surfaces for dental implants by chemically modifying their surface through the deposition of bioactive Ta1-xOx coatings deposited by DC magnetron sputtering. The influence of the oxygen partial pressure on the structure, morphology and topography of Ta-based films was analyzed. The coating’s bioactivity was evaluated by in vitro tests through the samples immersion in Simulated Body Fluid (SBF).

Chemical composition, deposition parameters, deposition rate and critical load of the deposited samples.

### Table 1

<table>
<thead>
<tr>
<th>Sample</th>
<th>Chemical formula</th>
<th>Chemical composition (at.%)</th>
<th>O2 Flow (sccm)</th>
<th>Current density (mA/cm²)</th>
<th>Deposition rate (μm/h)</th>
<th>Critical load (LC3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ta1</td>
<td>Ta46O33</td>
<td>95 ± 0.3</td>
<td>5 ± 0.3</td>
<td>0</td>
<td>10</td>
<td>&gt;80 N</td>
</tr>
<tr>
<td>T01</td>
<td>Ta46O33</td>
<td>89 ± 0.6</td>
<td>11 ± 0.6</td>
<td>2</td>
<td>10</td>
<td>2.3</td>
</tr>
<tr>
<td>T03</td>
<td>Ta57O32</td>
<td>72 ± 0.2</td>
<td>27 ± 0.2</td>
<td>6</td>
<td>10</td>
<td>2.3</td>
</tr>
<tr>
<td>T05</td>
<td>Ta66O14</td>
<td>57 ± 0.2</td>
<td>43 ± 0.2</td>
<td>10</td>
<td>10</td>
<td>2.8</td>
</tr>
<tr>
<td>T06</td>
<td>Ta46O33</td>
<td>30 ± 0.4</td>
<td>70 ± 0.4</td>
<td>13</td>
<td>5</td>
<td>1.9</td>
</tr>
</tbody>
</table>

Coating chemical composition was determined in a Cameca SX50 electron probe microanalysis (EPMA) equipment, operating at 10 kV and 40 nA. Scanning electron microscopy (SEM) was used to measure the film thickness and evaluate the coating morphology. SEM analysis was performed using a LEICA S360 operating at 10 kV in secondary electron mode. The structure and phase distribution of the films were determined by X-ray diffraction (XRD), in a Bruker D8 Discover, operating at 40 kV and 40 mA, with Cu radiation (λCuKα1 = 0.1540600 nm and λCuKα2 = 0.1544339 nm), equipped with collimator. The experiments were carried out in grazing angle geometry (1°). All the tests were performed with a step size of 0.025° and a time per step of 2 s, in 10–80° range. The morphology/topography of the coatings was evaluated by atomic force microscopy (AFM) using a NanoScopell model from Digital Instruments operating in tapping mode. AFM images were taken over scanning areas of 5 × 5 μm² and, for each film, three different areas were analyzed. EPMA, SEM and XRD analysis were performed in coatings deposited onto Si substrates since it allows an easier and more accurate characterization. In fact, its very low roughness surface improves the homogeneity of the sample to be tested improving the reproducibility of the measurements. We are aware that the final products will not have this final finishing surface, but for comparison and optimization purposes, it is important to keep this homogeneity, AFM measurements were performed in coatings deposited onto Si and SS 316L substrates.

The adhesion between Ta1-xOx coating and the substrate, SS 316L, was assessed by scratch test experiments using a Mikron VCE 500 equipment. For all samples, two scratch tests were performed using a diamond Rockwell indenter. The load was increased linearly in the range of 2–90 N with a rate of 10 N/min and a sliding speed of 10 mm/min. The critical load values (LC3) were determined by optical microscope observation of the scratch tracks. The critical loads correspond to severe delamination when more than 50% of the substrate is exposed [34].
2.3. Wettability measurements

Wettability is an important surface property of biomaterials that can regulate the protein adsorption and, subsequently, the cell behavior [35]. This paper follows the Van Oss approach [36] to characterize the samples surface as a hydrophilic or hydrophobic. Van Oss considers that a surface with contact angle above 65° is hydrophobic, while for values lower than 65° the surface is considered hydrophilic. Moreover, the calculation of the free surface energy (∆Gmwm) also allows to classify quantitatively the hydrophilic/hydrophobic character of a surface. The surface free energy is the necessary work to expand the drop of liquid on a unit of area. In this case, when the surface free energy is negative the interaction between the molecules of the liquid and the surface of the sample is attractive and, thus, the surface poorly interacts with water, making it hydrophobic. Conversely, when the free surface energy becomes positive (≥0), the interaction is repulsive and, consequently, the surface is hydrophilic due to the higher interaction between the sample surface and the water. Therefore, zero free surface energy is the border between hydrophilic and hydrophobic surfaces [36].

The wettability characteristics of the surfaces were assessed by measuring the static contact angle in a DataPhysics OCA-15 apparatus with Oss approach [36]. The calculation of coating hydrophobicity parameters using the Van Oss approach allows to statistically validate the results. SEM and energy dispersive X-ray spectroscopy (EDS) (NanoSEM – FEI Nova 200 (SEM); EDAX – Pegasus X4M (EDS) operating at 5 and 10 keV in secondary electron mode and in EDS mode, respectively) were used to study and characterized by cauli flower-like patterns, which generally are observed in coatings grown with typical columnar morphologies. The coatings with higher oxygen contents showed smoother surfaces (see Table 2), while the coatings with lower oxygen contents showed rougher surfaces. The slight increase in roughness values of the coatings with higher oxygen contents showed smoother surfaces with lower roughness. The slight increase in roughness values of the coatings deposited in compound mode might be related with the different deposition parameters: decrease in JTa and increase in O2 flow (see Table 1).

3. Results

3.1. Physical and chemical characterization

Coating deposition parameters, their chemical composition and thickness are summarized in Table 1. When the oxygen (O) flow was increased from 0 sccm up to 10 sccm an increase in the oxygen content from 5 to 43 at.% was observed. The oxygen in the Ta coating could be attributed to residual O2 present in the deposition chamber. Concerning the deposition rate, no significant changes were observed with increasing O2 flow up to 10 sccm. As target potential values also do not change significantly (from 349 to 416 V), the depositions are still being performed in metallic mode. In order to further increase the oxygen amount in the coating, the JTa was reduced from 10 mA/cm² to 5 mA/cm² and the O2 flow was set to 13 sccm. The increase in target potential value (537 V), in spite of the much lower target current used in the deposition, suggests that the coating was now deposited in compound mode, reaching an oxygen content of 70 at.%.

For application in biomedical devices, coating adhesion onto the implant is an important characteristic to be considered. Scratch testing results revealed a remarkable adhesion behavior for all coatings taking into account that a soft steel substrate is being used (SS 316L). In fact, the critical load values are higher than 80 N in all tested samples.

3.2. Structural analysis

XRD analyses were carried out in order to understand the evolution of the structure with the increase of the oxygen content. The XRD patterns are shown in Fig. 1 and the main identified crystalline phases are α-Ta: body-centered cubic (bct) (ICDD card n° 00-004-0788) and β-Ta: tetragonal (ICDD card n° 00-025-1280). The differences in the chemical composition correlated well with the differences observed in the developed structure.

Ta1 coating crystallized in a bcc which represents the typical structure of α-Ta. When oxygen was added to Ta, a change in the bcc structure to a mixture of α-Ta (bct) and β-Ta (tetragonal) was achieved. With further addition of oxygen, XRD peaks enlarges and becomes less defined suggesting that Ta phases became nanocrystalline. Still, oxides phases such as bcc Ta2O (ICDD 01-074-2305), tetragonal TaO2 (ICDD card n° 00-019-1297) and/or TaO5 (Orthorhombic ICDD card n° 01-070-4776) cannot be disregarded since they also have diffraction lines centered in the main broad peak (see Fig. 1b). The coating with 70 at.% of oxygen deposited in reactive compound mode revealed an amorphous structure, as suggested by the absence of diffraction peaks in the XRD pattern.

3.3. Morphology and topography assessment

The morphology and topography of each coating was analyzed by SEM and AFM, respectively, and the results are depicted in Fig. 2. In general the films revealed fairly uniform deposition. The AFM results are very well correlated with the surface morphology disclosed by SEM images. The AFM and SEM micrographs of Ta1 and TO1 coatings are characterized by cauliflower-like patterns, which generally are observed in coatings grown with typical columnar morphologies. The coatings with higher amounts of oxygen showed a smooth surface which is typical of very compact coatings with featureless morphology.

The roughness values obtained from AFM analysis of coatings deposited on Si substrates are shown in Table 2. The increase of oxygen content on the coatings promotes a significant decrease of the mean roughness values. Ta1 and TO1 coatings showed similar topographies/ morphologies with very similar roughness values (see Table 2), while the coatings with higher oxygen contents showed smoother surfaces with lower roughness. The slight increase in roughness values of the coating deposited in compound mode might be related with the different deposition parameters: decrease in JTa and increase in O2 flow (see Table 1).

The roughness values of CT Ti Gr2 (used in commercial dental implants) and SS 316L bulk materials as well as Ta1-xOx coatings deposited on SS 316L substrates are shown in Table 3. The roughness of the coatings deposited onto SS 316L follows the same trend as the coatings deposited on Si substrates (see Table 2), with slightly higher values, attributed to the higher roughness of the substrate.
3.4. Wettability analysis

The measured contact angle values and the surface free energy of the samples are presented in Table 4. CP Ti Gr2 was used as the commercial surface control.

In view of Milli-Q water, Ta1 surface has a much higher contact angle (around 100°) than the control CP Ti Gr2 (approximately 74°) being assumed as the sample with the most hydrophobic character. With the increase of oxygen content in the coatings a decrease of the contact angle values was observed with values from 81° down to 63°.

Regarding the surface free energy values, similar trends were observed, Ta1 coating showed the lowest free surface energy (−97 mJ/m²), less than the CP Ti Gr2 control. Oxygen-containing coatings have increasing free surface energies, in the range from −65 mJ/m² up to −31 mJ/m², with increasing oxygen contents. All analyzed samples showed a typical hydrophobic behavior (with a surface energy value below zero). TO6 surface has the highest value of surface free energy, thus, indicating a lower degree of hydrophobicity, which is in accordance with its contact angle value slightly below 65° (63°). These results suggest that TO6 sample has some polar interaction with the liquids.

3.5. Bioactivity response

In order to analyze the osteoconductive response of the studied materials and their potential for use in bone tissue replacement of dental implants, bioactivity tests were performed in SBF. The bioactive character allows to analyze the ability for apatite formation at the material surface after immersion in SBF, which intends to simulate the human blood. The bioactivity tests were performed in three samples, CP Ti Gr2, Ta1 and TO6; the first serving as standard and the two coatings which presented the threshold values measured for the contact angle and the surface free energy.

Fig. 3 shows SEM micrographs of the surfaces of the three studied samples before and after immersion in SBF for 14 days. Note that the results for samples before soaking in SBF are, hereafter, denoted as 0 h. The SEM micrographs show the different morphology of the calcium phosphate formed on the surfaces after 14 days of immersion in SBF.

The presence of Ca and P was verified by EDS technique, the mean ratio Ca/P was determined by the average of three EDS measurements in different zones of the sample. It should be pointed out that before 7 days, no calcium phosphates was detected in any of the analyzed surfaces. After 7 days only for the CP Ti Gr2 sample signs of calcium phosphates were not observed. After 14 days of exposure the Ca/P atomic ratio on the surface of the coating with 70 at.% oxygen, TO6, was 1.73 approaching the ratio of natural hydroxyapatite (1.67 according to the literature [38]). Calcium phosphates were also observed on the Ta1 surface, with a ratio Ca/P close to the natural hydroxyapatite (1.57). The CP Ti Gr2 control showed the worst bioactive behavior since, by EDS, the calcium phosphates visible in the surface show a Ca/P ratio very far from the natural hydroxyapatite, specifically 0.95.

Fig. 4 shows the XRD results of the immersed samples in SBF after 14 days. Ta1 and TO6 samples showed the presence of a crystalline phase based on calcium phosphates as suggested by EDS results. This apatite is strongly oriented, not being detected any other XRD peak in the diffractogram, which does not allow to precisely identify which apatite structure in being formed. The crystallinity degree is significantly higher in Ta1 than for TO6 surface. On the other hand, CP Ti Gr2 only showed peaks corresponding to the hexagonal Ti phase (ICDD card n° 00-044-1294) suggesting that the formed calcium phosphates in its surface is in very low amount.

![Grazing incidence XRD patterns of the coatings as a function of the oxygen content, deposited onto Si substrates.](image)
Fig. 2. SEM and AFM micrographs of Ta$_{1-x}$O$_x$ coatings as a function of the oxygen content, deposited onto Si substrates.
4. Discussion

4.1. Coating production

The elemental chemical composition showed, as it would be expected, that by increasing the O2 flow, the oxygen content increases from 5 up to a maximum value of 70 at.%. The oxygen in Ta1 film is attributed to residual O2 in the deposition chamber. Concerning the deposition rate, up to O2 flows of 10 sccm, the incorporation of oxygen in the growing film leads to higher values. However, when the current density changes to 5 mA/cm² and the O2 flow was set to 13 sccm, the deposition rate decreased dramatically, due to the marked reduction of the sputtering yield of the target either related to the reduction of current density (half of value) or to the poisoning effect of the target. This behavior is similar to that achieved by Chandra et al. [39] in the deposition of tantalum oxides coatings, Cristea et al. [40] in TaON films or Vaz et al. [41] in ZrON coatings, in all cases deposited by reactive sputtering.

XRD revealed the body-centered cubic phase, α-Ta, for Ta1 coating. According to Chandrasekhar et al. [42] the occurrence of this phase at relatively low deposition temperatures, compared to the results of other authors [28], is explained by the application of negative bias during the deposition. When the oxygen content increased to 11 at.%, the crystal structure changed to a mixture of α-Ta and β-Ta phases. This behavior was also observed by Zhou et al. [43,44] in the Ta-O system for reactive sputtering with low O2/Ar flow ratio. According to Kepner et al. [45] the incorporation of oxygen in the coating leads to a distortion in the structure of α-Ta phase (stable phase), due to its low solubility in this phase (≤ 1.4 at.%), promoting the formation of β-Ta phase [45]. For films with intermediate oxygen content (TO3 and TO5) the broad diffraction band at 37° suggests that the coating is nanocrystalline making difficult an unequivocal identification of the phase or phases occurring. In fact, in this zone, diffraction peaks of tantalum and sub-stoichiometric tantalum oxide phases, such as α-Ta, β-Ta, Ta2O5, TaO2, and/or Ta2O3 phases may occur. Yang et al. [31] also reported this band on tantalum oxide coatings deposited by reactive sputtering. With increasing oxygen content, there is a shift of the band to the left that can be associated with the increase of the inter-atomic distance induced by the presence of further oxygen species.

The coating with the highest oxygen content was amorphous. This behavior is usually observed for other oxygen-containing compounds deposited by reactive magnetron sputtering as, for example, W–O [46], W–O–N [47], TiC0.5O [48] and Ti–Si–C–N–O [49]. According to the literature [50], the incorporation of oxygen in the crystal lattice causes the deformation of the initial metal structure promoting initially the precipitation of oxides in the grain boundaries, inhibiting the grain growth and decreasing the grain size, and leading, in a second step, to the formation of amorphous structure [50].

The cauliflower-like patterns developed by Ta1 and TO1 coatings are characteristic of coatings grown with low adatom mobility and relatively high discharge pressures, with typical columnar morphologies [51]. TO1 film shows sharp edges particles over the coating surface. This morphology, according to Zhou et al. [43], is related with the mixture of α and β Ta phases, which is in good agreement with XRD results. The surface micrographs (see Fig. 2) show that the increase in oxygen content promoted the coating densification, showing the smooth surface typical of very compact and cross section featureless coatings. These results are confirmed by AFM analysis, which showed decreasing Ra and Rq roughness values with increasing oxygen content. Banakh et al. [52] observed the same trend in TaON coatings deposited by reactive sputtering. In other similar systems as W–O [53] and W–O–N [47] this behavior was also found.

4.2. In vitro behavior

Surface wettability is an important parameter which should be taken into account for tissue engineering applications [54]. This physicochemical property does not affect directly the cell response, but can regulate the adsorption of the most important proteins from the culture medium, such as fibronectin and vitronectin, which will mediate the cell response and improve the cell adhesion [55]. As reported, moderately hydrophobic (70–60°) surfaces tends to adsorb the adhesion-promoting proteins (fibronectin and vitronectin) which will improve the cell attachment [56].

The contact angle tests showed that Ta1 surface has the highest value, around 100°, then presenting the most hydrophobic character (θ > 65°). The increase of oxygen content on the coatings caused a decrease of the contact angle, due to the growing oxidation of the films, as it was shown by Sharma and Paul [57].

From literature [27], based on the surface chemistry, for Ta1 sample a lower contact angle in relation to control surface, CP Ti Gr2, was expected (31° and 54° respectively). Such trend was not observed in this study. This discordant result can be explained by the significant difference in the roughness values of the tested samples. In fact, the commercial control sample has a much higher Ra value than Ta sample, factor which is known to have a great influence on the contact angle [58–60]. According to the literature [36], for Ta1–xOx coatings, at the observed levels of roughness the influence on the wettability is not clear. Therefore, these results suggest that the surface chemistry (increase of the oxygen content) is predominant on the regulation of the wettability.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Contact angle ± SD (deg)</th>
<th>Surface energy components (mJ/m²)</th>
<th>ΔG_renew (mJ/m²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CP Ti Gr2</td>
<td>74 ± 2.8</td>
<td>48 ± 3.1</td>
<td>25 ± 1.4</td>
</tr>
<tr>
<td>Ta1</td>
<td>100 ± 4.8</td>
<td>67 ± 3.9</td>
<td>36 ± 1.5</td>
</tr>
<tr>
<td>TO1</td>
<td>81 ± 2.9</td>
<td>47 ± 3.1</td>
<td>23 ± 4.1</td>
</tr>
<tr>
<td>TO3</td>
<td>70 ± 1.7</td>
<td>50 ± 2.0</td>
<td>28 ± 1.7</td>
</tr>
<tr>
<td>TO5</td>
<td>71 ± 2.8</td>
<td>49 ± 1.9</td>
<td>24 ± 0.75</td>
</tr>
<tr>
<td>TO6</td>
<td>63 ± 2.8</td>
<td>38 ± 3.5</td>
<td>21 ± 0.98</td>
</tr>
</tbody>
</table>

* Standard deviation.

Table 3

<table>
<thead>
<tr>
<th>Sample</th>
<th>CP Ti Gr2</th>
<th>SS 316L</th>
<th>Ta1</th>
<th>TO1</th>
<th>TO3</th>
<th>TO5</th>
<th>TO6</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ra (nm)</td>
<td>71 ± 39</td>
<td>25 ± 0.11</td>
<td>21 ± 2.2</td>
<td>21 ± 1.8</td>
<td>7.8 ± 0.61</td>
<td>5.1 ± 0.57</td>
<td>5.8 ± 0.40</td>
</tr>
<tr>
<td>Rq (nm)</td>
<td>88 ± 49</td>
<td>1.4 ± 0.25</td>
<td>26 ± 2.6</td>
<td>31 ± 2.6</td>
<td>9.5 ± 0.77</td>
<td>6.4 ± 0.69</td>
<td>8.2 ± 0.53</td>
</tr>
<tr>
<td>Rmax (nm)</td>
<td>503 ± 250</td>
<td>44 ± 3.1</td>
<td>201 ± 6.3</td>
<td>305 ± 42</td>
<td>109 ± 28</td>
<td>54 ± 5.9</td>
<td>103 ± 17</td>
</tr>
</tbody>
</table>

Table 4

<table>
<thead>
<tr>
<th>Sample</th>
<th>Contact angle ± SD (deg)</th>
<th>Surface energy components (mJ/m²)</th>
<th>ΔG_renew (mJ/m²)</th>
</tr>
</thead>
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<td>70 ± 1.7</td>
<td>50 ± 2.0</td>
<td>28 ± 1.7</td>
</tr>
<tr>
<td>TO5</td>
<td>71 ± 2.8</td>
<td>49 ± 1.9</td>
<td>24 ± 0.75</td>
</tr>
<tr>
<td>TO6</td>
<td>63 ± 2.8</td>
<td>38 ± 3.5</td>
<td>21 ± 0.98</td>
</tr>
</tbody>
</table>
Both polar surface energy components ($\gamma^+$ and $\gamma^-$) of Ta1 and TO1 samples are close to zero which indicates that the surface is predominantly apolar. However, with the increase of oxygen content, the negative polar surface energy component ($\gamma^-$) starts to increase significantly, indicating that the surfaces become monopolar. All samples showed qualitatively a hydrophobic behavior in agreement with their low surface energy, excepting the coating with the highest oxygen content (TO6) which showed a contact angle value slightly below of $65^\circ$ ($63^\circ$). This value is indicative of polar surface interaction typical to moderately hydrophilic surfaces. A better cell adhesion to hard tissue (bone) is expected for this sample since, for moderately hydrophilic and negatively charged surfaces the adsorption of cells is enhanced [54,61,62]. Bacakova et al. [61], showed that a contact angle close to $63^\circ$ is an optimum value for osseointegration.

Ta$_{1-x}$O$_x$ samples showed better ability to change and adsorb ions of SBF and, consequently, better bioactivity performance comparatively to the group control CP Ti. After 14 days of immersion in SBF, both Ta-based surfaces showed Ca/P values close to that of hydroxyapatite (Ca/P $\approx$ 1.67), particularly the oxide coating with a value of 1.73. The commercial surface control of CP Ti Gr2 shows the lowest Ca/P ratio suggesting that the osseointegration process should be slower. This fact proves that the bioactivity kinetics of Ta$_{1-x}$O$_x$ surfaces is faster than that of Ti surface favoring a faster osseointegration.

In the oxide sample the adhesion of ions of the fluid, namely Ca$^{2+}$, to the surface of the sample was significantly superior, what was expected since this sample showed a surface free energy close to zero and a lower contact angle around $63^\circ$, reported as optimum conditions for osseointegration. According to Kokubo et al. [63,64], oxide surfaces are the best option for the interaction with the fluid. From literature [24], when a Ta oxide (such as TO6) surface is soaked in SBF, by ion exchange, hydration of Ta–O occurs and Ta–OH groups are formed, providing favorable sites for the calcium phosphates nucleation. The Ta–OH groups bind to Ca$^{2+}$ ions forming a tantalate which, then, binds to PO$_4^{3-}$ ions to form apatite. The bone progenitor cells interact with the oxide phase through this diffusion layer; the chemical bonding established between the functional groups (Ta–OH) and the calcium phosphate ions promotes a stronger bond between the dental implant surface and the cells. As verified, the Ta–OH groups induce a faster apatite nucleation by increasing the ionic activity at the surface. Therefore the oxidation state of the surface is beneficial for the exponentiation of osseointegration [24].

Ta1 sample also demonstrated a high ability to bind with calcium phosphate ions even though only a residual content of oxygen exists. The high passivation rate of Ta and the oxide layer formed on the top [57] have a fundamental role for the formation of Ta–OH groups when the sample is soaked in SBF. For the control surface, CP Ti Gr2, although

Fig. 3. SEM micrographs of studied samples, CP Ti Gr2, Ta1 and TO6, respectively, before and after 14 days of immersion in SBF at 37 °C.
Ti also has a high passivation rate [65], it does not so easily promote apatite formation. The surface chemistry of Ta-based and Ti-based surfaces is different which, as reported by Frandsen et al. [27], causes a significant difference in the adhesion of the calcium phosphate ions.

Concerning the Ca/P atomic ratio estimated by EDS, it is possible to observe that there is a difference between the values of Ta1 sample and TO6 sample. These differences can be explained by the presence of carbon in the calcium phosphates, as detected by EDS measurements. As it is known, apatite is a flexible mineral that needs several elements to grow, such as, Ca, P, O and the appropriated channel-filling ions (OH−, Cl−, F−, CO3−2) [66]. Subsequently, these ions allow several chemical substitutions determining the apatite structure. Usually the bone is an OH− containing apatite with a very specific structure and composition [38]. According to the literature [67], the biomimetic way to induce the apatite growth as proposed by Kokubo and Takadama [37], also used in this study, leads to a carbonate containing bone-like apatite [67]. The carbonate substitution in the apatite structure can occur through 2 different ways: in the OH-site as “A-type” substitution; or in the PO4-site as “B-type” substitution. Hence, it is suggested that in the present study the differences of the Ca/P atomic ratio values are related to the type of C substitution, in Ta1 surface should be of A-type whereas for TO6 of B-type [38].

After 14 days of immersion, the changes in the morphology of the calcium phosphates of the soaked samples is mainly dictated by the Ca/P ratio. The morphology of the calcium phosphate in the control surface is a typical cauliflower-like apatite cluster [68] whereas, in the Ta1-xOx surfaces the morphology of the calcium phosphates evolve to a needle shaped-like apatite [69,70]. These needles are composed by a lot of densely packed lamellas of crystalline apatite [67]. This morphology is very promising since it is similar to that of the apatite which constitutes the bone [70].

The XRD results (see Fig. 4) are not conclusive since only one peak, around 33.86°, is detected in the pattern. However, considering the chemical composition estimated by EDS, showing the presence of carbon on the calcium phosphates, this peak can be assigned to either a monoclinic calcium phosphate carbonate (ICDD card n° 00-035-0180) or a monoclinic calcium tetraphosphonate dehydrate (ICDD card n° 00-025-1996). The lower crystallinity degree of TO6 sample can be related with the above type of carbonate substitution in the apatite structure. In fact, in the B-type substitution suggested for the Ta oxide sample, the amorphous carbonate is incorporated into the apatite structure in the PO4-site, which can leads to a decrease of the apatite crystallinity. The XRD pattern of the commercial control surface, CP Ti Gr2, only shows peaks corresponding to the hexagonal Ti phase which suggest that the presence of calcium phosphates in the surface is very low and, therefore, undetectable by XRD.

5. Conclusion

Ta1-xOx coatings with different oxygen content were successfully deposited by reactive magnetron sputtering. Structural analysis revealed that the coatings with low and intermediate oxygen content showed a mixture of Ta and Ta (sub)oxide phases with a nanocrystalline structure; while the coating with the highest oxygen content proved to be amorphous. The increase in the oxygen amount retrieved more compact and smoother Ta1-xOx coatings. Contact angle measurements revealed that Ta1 coating presented the most hydrophobic character (100°). Besides, the increase of oxygen content caused the decrease on the contact angle values with TO6 coating depicting the lowest value, about 63°. Bioactivity tests showed the presence of calcium phosphates after 7 days of immersion in SBF, only for Ta1-xOx samples. This behavior was confirmed after 14 days of exposure since Ca/P ratio values of 1.57 and 1.73 were measured for Ta1 coating and TO6 coatings, respectively, close to the hydroxyapatite value (Ca/P ≈ 1.67). The commercial surface control CP Ti Gr2 showed a much lower Ca/P ratio of 0.95, meaning that the osseointegration was not well enhanced as for the promising Ta1-xOx whereas surfaces.

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Fig. 4. XRD patterns of CP Ti Gr2, Ta1 and TO6 surfaces, respectively, after 14 days of immersion in SBF at 37 °C.


