Microstructural investigation of porous titanium coatings, produced by thermal spraying techniques, using plasma atomization and hydride-dehydride powders, for orthopedic implants

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ABSTRACT

The present study focuses on porous titanium (commercially pure Ti) coatings for future use on medical implants, manufactured by specific thermal spray method. Its objective is to investigate the possibility of Ti porosity to offer room for medication storage in addition to bone growth promotion. Three specimens for each different type of coating were produced by different sets of thermal spray process/feedstock powder, namely, (1) Flame Spray (FS) with spherical Plasma Atomization (PA) powder, (2) Atmospheric Plasma Spray (APS) with spherical PA powder and (3) APS with angular Hydride – Dehydride (HDH) powder. The specific types of specimens along with the two powders produced by the PA and HDH processes were characterized using various techniques, namely (a) Roughness measurements of the coated surfaces and thickness measurements of the coatings, which disclosed the highest values for the FS-PA coating, Ra = 11.19 ± 0.21 μm and average thickness of 281 μm, (b) Optical microscopy and SEM-EDS to study the surface morphology and microstructure of the coatings and discover any possible oxidation or other phases. The porosity percentage was measured and the pore size distribution was also estimated. The porosity percentages of the coatings ranged from 12% on the APS-PA coating to 34% on the FS-PA coating, (c) XRD analyses which showed varying titanium oxide formations for each type of specimen. These oxides may prove to be beneficial for the development of osseous tissue, (d) assessment of biological response of the coatings in vitro that resulted in satisfactory primary response in a physiological environment and the formation of calcium phosphate phases with Ca/P ratio of 1.61 and (e) Vickers microhardness measurements, which resulted in values that fluctuated from 786.6 for the FS-PA coating to 967.6 for the APS-HDH coating. Overall, the produced FS-PA coating is characterized by high porosity content and satisfactory bioactivity, in order to fulfill the objective of the project for biomolecule incorporation and drug storage.

1. Introduction

Pure titanium and its alloys are among the most attractive materials for biomedical applications and are most commonly used as implants for orthopedic reconstruction and dental restoration, due to the excellent physical and chemical properties of titanium. The drawback titanium displays in its clinical practice, is the mismatch of its Young’s modulus (105 GPa [1]) with that of the surrounding bone tissue (10–30 GPa [1]), which is the main reason for implant loosening following stress shielding [1].

Implant porosity, especially in the form of interconnected pores, has positive impact on bone neoformation in vivo, since it increases the contact area between the porous surface of the implant with the bone tissue, thus resulting in improved implant stability over time. The porous structure must have a high porosity percentage, to promote spatial bone growth and cell adhesion, since osteoblasts behave differently depending on the pore size. According to Karageorgiou and Kaplan [2], the minimum pore size should be 100 μm, considering the cell size and the characteristics of cell migration and transport. Yet the formation of capillaries is accelerated when the pore size reaches approximately 300 μm. Takemoto et al. [3], suggested that the percentage of surface layer pores for Ti implants should reach 40%, while other

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researchers were more tolerant, suggesting a porosity content in the range of 25–66% [4]. High percentage of porosity facilitates the transport of fluids, the formation of capillaries and promotes the formation on new bone tissue, though the mechanical properties are diminished due to the induced stresses [5]. In addition, inhomogeneity in the distribution of pores and the existence of pore cells with locally thin walls, throughout the implant coating, can lead to a reduction in materials strength and cause early fatigue failure [6]. Thereby, the need to maintain high mechanical properties of the implant, while providing adequate porosity for the proliferation of new vasculature, is crucial.

Another problem associated with medical implants that affects the medical community in the surgical field worldwide in the last decades, is the increasing number of antibiotic resistant bacterial pathogens, among which, biofilm-associated pathogens. Approximately 60% of the human infections are attributed to microorganisms able to form biofilms and thus, avoid the actions of antibiotics and the immune system. In this way, a reaction of the immune system is promoted, giving rise to inflammation at the underlying tissue, even in the case that such colonizing microorganisms do not cause infection themselves. As a result, release of the implant is occurred and subsequent costly and painful implant removal and replacement is promoted. These surgical interventions entail an increase in antibiotic consumption, together with a release of the implant is occurred and subsequent costly and painful implant removal and replacement is promoted. These surgical interventions entail an increase in antibiotic consumption, together with a health cost of about 50,000–90,000 € per infection episode [7]. In the US only, nosocomial infections related to medical implants reach almost 50% of the estimated two million annual infections, with a total implying treatment cost of over $3bn.

To counteract the detrimental effects of biofilm infections onto the implanted prosthetic devices the European Commission “NOMORFILM: Novel marine biomolecules against biofilm” project is focused in the search of new marine biomolecules from microalgae presenting antimicrobial and antibiofilm activities [7]. These bioactive compounds will then be incorporated into porous biomaterials used in manufacturing of prosthetic implants, avoiding the replacement of these devices in patients affected by biofilm associated infections.

The present research was accomplished within the context of the NOMORFILM project. The novelty of this paper lies in the use of two different titanium powders regarding their microstructure and origins and also, in our attempt to produce titanium coatings with pores of decreased size in relation with those existing in the available commercial titanium implants, in order to make them suitable for drug storage. Flame Spray (FS) and Atmospheric Plasma Spray (APS) techniques were utilized in order to produce porous titanium coatings on stainless steel substrate. The specific techniques have been used before for deposition of pure titanium feedstock with resulting coating porosity of up to 10.2%, great enough for the incorporation of biomolecules [9]. The sprayed feedstock were two kinds of commercially pure (cp) Ti (100 wt%) powders, produced by two distinct processes, namely, Plasma Atomization (PA) and Hydride-Dehydride (HDH) process. The substrate was AISI 304 stainless steel and had previously been grit-blasted in order to clean the surface and create the necessary surface roughness for the coating to be mechanically interlocked. Three different coatings were produced by different combinations of thermal spray technique and powder type; (1) FS with PA powder, (2) APS with PA powder and (3) APS with HDH powder. The titanium coatings obtained with the specific sets of thermal spray process/feedstock powder, along with the two powders produced by the PA and HDH processes were subsequently characterized, regarding their porosity, roughness, thickness, microstructure and crystal structure.

2. Experimental procedure

2.1. Materials

Coatings on AISI 304 stainless steel substrate, were prepared with a commercially pure titanium porous coating, by means of FS and APS processes. Substrate’s preparation before thermal spraying included grit-blasting with Al₂O₃ grit (18–24 mesh), at 7 MPa, in order to clean the surface and create the necessary surface roughness for sufficient mechanical interlocking of the molten or semi-molten particles with the asperities of the roughened substrate. After ten measurements, the average and standard deviation values of the roughness parameters Ra and R₉₉₉₉ of the substrate were calculated as 4.17 ± 0.36 μm and 32.76 ± 2.70 μm, respectively, thus providing better adhesion between the substrate and the coating [10,11]. A METCO SII gun for FS and a SG-100 Praxair plasma gun for APS were used, both with a KUKA 6 axis robot. The process gases were Ar and H₂ with respective gas pressures of 50 and 14 psi. A total number of 8 passes were applied for the layering of titanium, at a gun speed of 450 mm/s. The powder flow rate, stand-off distance, current and voltage varied.

The two types of feedstock powder that were used, were both cp-Ti powders (100 wt%) and had been produced by the PA and HDH techniques. The powder produced by the PA process, exhibited a perfectly spheroid morphology (Fig. 1a) and was used in both the FS and APS processes. The powder produced by the HDH technique presented an angular morphology (Fig. 1b) and was used only in the APS process. The nominal particle size for both powders was ~75 + 45 μm. Three specimens for each different type of coating were produced by different sets of thermal spray process/feedstock powder, namely, (1) FS with PA powder, (2) APS with PA powder and (3) APS with HDH powder (Table 1).

Table 1

<table>
<thead>
<tr>
<th>Coating</th>
<th>Thermal spray process - powder</th>
<th>Commercial name</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Flame spray with PA powder</td>
<td>TiPYRO-1</td>
</tr>
<tr>
<td>2</td>
<td>Atmospheric plasma spray with PA powder</td>
<td>TiPYRO-1</td>
</tr>
<tr>
<td>3</td>
<td>Atmospheric plasma spray with HDH powder</td>
<td>TiMBN-1</td>
</tr>
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</table>

Fig. 1. SEM images of Ti powder (100 wt% Ti) produced by (a) PA technique with spheroid particles and (b) HDH technique, exhibiting an angular morphology.
2.2. Characterization techniques

Surface roughness was measured using TR-200 portable surface roughness tester of Time Group Inc. Ten measurements were taken and the following roughness parameters were evaluated: $R_s$ (arithmetic mean of the absolute departures of the roughness profile from the mean line) and $R_{\text{max}}$ (maximum peak-to-valley height of the profile).

The thickness of the porous titanium coatings was measured on cross sections of samples, by using Leica’s LAS Image Analysis. Measurements were performed at two distinct magnifications of 100 and × 200.

Furthermore, in order to analyze the porosity and microstructure of the coatings, samples of cross-sections were prepared using standard metallographic procedures. For better observational results, AISI 304 stainless steel was chemically etched with an etchant of HCl, HNO$_3$ and Glycerine in 3/2/1 ratio. Etching of titanium was also performed with the utilization of Kroll’s reagent, which is composed by 1.5 mL HF, 4 mL addition of Tris-hydroxymethyl aminomethane ((CH$_2$OH)$_3$CNH$_2$), values were recorded throughout the reaction and were adjusted by tentative analysis and was performed by the built-in software Di.

3.1. Porosity

The porosity area distribution is plotted in Fig. 2a to c. Analyses of porosity areas (in μm$^2$) of the cross-sections of the coatings were chosen, instead of number of pores, due to the irregular shapes of the pores. The coatings are constituted by heterogeneous pores with disparate pore sizes and consequently pore areas, as it is observed in the respective diagrams.

As it is shown, both types of specimens prepared with the APS technique (Fig. 2b and c), form porosity areas that do not exceed 5000 μm$^2$, while the FS-PA type of specimens (Fig. 2a) has a minimum porosity area of about 3000 μm$^2$ and also areas that reach approximately 63,000 μm$^2$. However, the fraction of the pores with an area in the range of 39,000–63,000 μm$^2$ is relatively small and constitutes roughly 10% of the total porosity. As it has already been determined in previous studies [14,15], significant osseointegration is not expected for pore sizes below 15,000 μm$^2$ (approximate effective diameter of 140 μm for circular pores), while according to other researchers, the optimal area of the pores is concluded to fall in the range of 10,800–21,500 μm$^2$ [15–17], which translates to an average effective diameter of 100–200 μm, in order for satisfying osseointegration to be achieved. Therefore, additional significant cell growth could only be expected, in the first type of specimen, in the fraction of the pores with an area in the range of 39,000–63,000 μm$^2$.

Table 2

<table>
<thead>
<tr>
<th>Number</th>
<th>Reactant</th>
<th>Quantity</th>
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</thead>
<tbody>
<tr>
<td>1</td>
<td>NaCl</td>
<td>9.8184 g</td>
</tr>
<tr>
<td>2</td>
<td>NaHCO$_3$</td>
<td>3.4023 g</td>
</tr>
<tr>
<td>3</td>
<td>KCl</td>
<td>0.5591 g</td>
</tr>
<tr>
<td>4</td>
<td>Na$_2$HPO$_4$</td>
<td>0.2129 g</td>
</tr>
<tr>
<td>5</td>
<td>MgCl$_2$·6H$_2$O</td>
<td>0.4574 g</td>
</tr>
<tr>
<td>6</td>
<td>HCl (1 M)</td>
<td>15 mL</td>
</tr>
<tr>
<td>7</td>
<td>CaCl$_2$·2H$_2$O</td>
<td>0.5531 g</td>
</tr>
<tr>
<td>8</td>
<td>Na$_2$SO$_4$</td>
<td>0.1065 g</td>
</tr>
<tr>
<td>9</td>
<td>Tris</td>
<td>9.0855 g</td>
</tr>
<tr>
<td>10</td>
<td>HCl (1 M)</td>
<td>50 mL</td>
</tr>
</tbody>
</table>

with 1.0 M hydrochloric acid (HCl), which redintegrated the pH to the desired value of 7.4. Each reactant was added to the solution with 10-minute intervals and the quantities of the reactants were chosen in order for the ionic concentrations in the solution to closely relate to those of human blood plasma. The reactants used for preparation of 1 L of the SBF solution are presented in Table 2, according to their order of introduction into the solution.

3. Results and discussion

3.2. Surface properties and coatings’ morphologies

During the APS process, oxidation usually occurs. High contents of titanium oxide and titanium nitride are often found in the APS-deposited titanium coatings, which arise from the reaction between the pure titanium feedstock with oxygen and nitrogen, present in the working gases or the surrounding atmosphere [18]. The gases used in plasma spraying are mostly the inert gases Ar and He, which can limit the oxide formation on the coating (Fig. 3b and c), in contrast to flame spray, that works usually with oxyacetylene or propane and develops a high percentage of oxidation which appears to darken the surface [19] (Fig. 3a).

Moreover, it has been reported that, surface topography (i.e. surface roughness) is in fact affected by chemical composition of the coating [20]. More specifically, if a cp-Ti coating surface is enhanced by a thicker (100 nm) oxide layer coating additionally to the naturally
grown thin Ti oxide layer, surface roughness parameters appeared to be somewhat elevated. The average values and standard deviations of the roughness parameters $R_a$ and $R_{max}$ and also the thickness of each type of coating, are presented in Table 3.

As it is observed, the roughest coating was the one fabricated by the FS technique, in which traces of oxidation were macroscopically evident and which had a mean roughness of $R_a = 11.19 \pm 0.21 \mu m$. The corresponding values of average roughness ($R_a$) for coatings 2 and 3 were $9.13 \pm 0.17 \mu m$ and $7.65 \pm 0.10 \mu m$. In addition, all coatings exhibited a uniform thickness of an average value of $281 \pm 20 \mu m$ for the FS coating, $239 \pm 8 \mu m$ for the APS coating with PA powder and $125 \pm 7 \mu m$ for the APS coating with HDH powder.

Regarding their surface characteristics, unmelted particles, re-solidified particles, oxide inclusions, pores and splats constitute the typical microstructure observed in all the coatings. More specifically, all the coatings presented a high porous non-homogeneity all over the surface. The typical lamellar (layered) structure is obvious at lower magnifications (Fig. 4a, d and g), from which a net of inter-lamellar pores between layered splats emerges. The porous net becomes clearly visible on the surface of the coating produced by FS with PA powder (Fig. 4a), as a consequence of the lower operating temperatures. Enough semi-molten and fewer unmelted particles are also discerned. A more dense morphology is observed for the coatings prepared by the APS technique, assigned to the elevated operating temperatures in reference with the FS-PA coating (Fig. 4d and g). In the APS-PA coating (Fig. 4d) some isolated pores are presented, while in the APS-HDH coating (Fig. 4g) traces of oxides and oxidized sites in addition to the observed pores are shown.

At higher magnification (Fig. 4b, c, e, f, h and i), the splats are well-flattened and form smooth surfaces with discernible boundaries. Upon these splats, semi-molten feedstock particles are noticed, the shell of which has been melted, but the core has been kept intact. Moreover, some of the individual feedstock particles became rounded but they did not coalesce during spraying. Instead, they were agglomerated into a larger particle and formed semi-molten agglomerations (Fig. 4e).

In addition, some unmelted particles or fractions of particles that were shattered upon impact with the underlying as-sprayed material are dispersed on the surface of the coatings. It is noted that despite the angular morphology of the starting HDH powder, the unmelted particles or fractions of particles on the surface of the APS-HDH coating have become spherical (with partial size reduction). Thus, the characteristic porous microstructure in plasma spray coatings is limited compared to that of the FS-PA coating, enhancing intra-splat cohesion (Fig. 4i).

Furthermore, a few intra-splat microcracks and elongated micro-cracks, with a tendency to propagate (Fig. 4b, c, i), were also found in the surface of the coatings. These cracks are produced during the spraying process, denote high tensile stress in the coatings during the cooling and might play a significant role in the cohesion of the coatings.

Formation of oxides and reaction sites were also observed (Fig. 4g and h). Such phenomena are quite common in the APS-deposited titanium coatings, because of its sensitivity and high chemical reactivity with the surrounding gases and atmosphere. Nonetheless, oxides were traced on the surface of the FS-PA coating, despite the lower operating temperatures (Fig. 4c).

EDS spot analysis performed on the surfaces of the coatings revealed the existence of O and Ti, as expected, with the most dominant element being O against Ti, thus denoting oxidation of the surfaces. EDS spot analysis of a surface formation on one of the coatings prepared with the HDH powder, also detected Ca in a very small percentage (2.26%), apart from the already mentioned O and Ti. However, Ca is used in HDH powders in order to deoxidize them, hence its presence in the coating's surface is understandable.

After immersion of the specimens into the SBF solution for 7 days, a limited growth of calcium phosphate crystals is noted on the surface of the specimens, though most of the surface of titanium is not coated (Fig. 5a and d). Partially degraded salt crystal residues originated from
the SBF solution are also present on the surfaces of the coatings (Fig. 5g). At higher magnification, larger agglomerations of calcium phosphate particles are observed at the inside of existing cavities and pores on the coating surfaces, which act as nucleation and growth sites for the calcium phosphate particles (Fig. 5b and e). Calcium phosphate phase have also started to precipitate near salt residues (Fig. 5g and h).

At even higher magnification (Fig. 5c, f and i), the structure of the agglomerated particles is observed. The agglomerated particles consist of spheroid globules with typical size of about 1 μm or less (Fig. 5i). The existence of nuclei that belong to the nanoscale is an indication of poor crystallization of this preliminary calcium phosphate phases [21].

After immersion of 14 days into the SBF solution the retrieved specimens presented a slightly different surface morphology. Small precipitates seem to cover the whole surfaces of the coatings. Although these particles do not form a coherent layer over the sprayed titanium coatings, they are evenly dispersed all over their surfaces (Fig. 6a, d and g). In higher magnification (Fig. 6b, e and h), it is noted that these particles form clusters and even seem to emerge underneath the surface of the remaining salt residues from the SBF solution. Even higher magnification of these clusters, reveal that they are actually comprised of particles of less than 0.5 μm in size (Fig. 6c, f and i).

EDS spot analyses on the surfaces of the coatings that were immersed in the SBF solution for 14 days, revealed the presence of calcium, phosphorus, carbon, oxygen, and sodium. The presence of calcium and phosphorus is indicative of the formation of calcium phosphate. The presence of oxygen suggests the presence of water, which is consistent with the SBF solution. The presence of sodium is consistent with the presence of salt residues from the SBF solution.

Table 3
Average surface roughness, average coating thickness (in μm) and microhardness values of porous titanium coatings.

<table>
<thead>
<tr>
<th>Coating</th>
<th>Roughness (μm)</th>
<th>Thickness (μm)</th>
<th>Microhardness (HV 0.3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>11.19 ± 0.21</td>
<td>33.33 ± 0.50</td>
<td>281 ± 20</td>
</tr>
<tr>
<td>2</td>
<td>9.13 ± 0.17</td>
<td>28.80 ± 0.79</td>
<td>239 ± 7</td>
</tr>
<tr>
<td>3</td>
<td>7.65 ± 0.10</td>
<td>23.78 ± 0.48</td>
<td>125 ± 7</td>
</tr>
<tr>
<td></td>
<td>R_max</td>
<td></td>
<td>786.6 ± 299.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>834.6 ± 131.3</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>967.6 ± 156.4</td>
</tr>
</tbody>
</table>

Fig. 3. Surface macrographs of (a) FS coating with PA powder, (b) APS coating with PA powder and (c) APS coating with HDH powder. The FS coating with PA powder appears to be darker than the others, possibly due to oxidation.

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<td>967.6 ± 156.4</td>
</tr>
</tbody>
</table>

Fig. 4. SEM micrographs of the surface of (a), (b), (c) FS-PA coating, (d), (e), (f) APS-PA coating and (g), (h), (i) APS-HDH coating, taken at different magnifications.
immersed in the SBF solution for 7 days, revealed the presence of K, Cl, Na and Mg, apart from the expected Ca, P and O elements, due to contact with the SBF solution. However, Ca/P ratio was very different to that of stoichiometric hydroxyapatite, implying that residence time into the SBF short and not adequate to completely cover the whole surface of the substrate. Finally, due to incomplete coating of the surface with hydroxyapatite, Ti element was also detected during EDS spot analyses. It is worth noting that, EDS spot analyses performed on the coatings after 14 days of immersion into the SBF solution, disclosed Ca/P ratios around 1.39. For the FS-PA coating the Ca/P ratio for the particles shown in Fig. 6c is 1.61, which is probably referred to a bi-phasic calcium phosphate, also known as a HAP/β-TCP combination.

3.3. Coatings’ microstructure

The typical lamellar microstructure of pure Ti based coatings obtained is shown in Fig. 7a, d and g. The coating manufactured with APS and PA powder (spherical) presented the greatest density. This occurred because the fine spherical particles of the powder feedstock were very well heated and deformed to a very good state of lamellae, so as they filled the spacing between the coarser particles. Careful selection of the spraying parameters and also, the nature of the specific spraying procedure contributed to this outcome. Despite notable density of the specific coating, some interconnected and isolated pores were formed, providing a porous matrix. Independently of the morphology of the feedstock powder used, during APS process the fine particles were heated, deformed into thin lamellae (splats), flattened and rapidly quenched upon impact with the substrate and therefore, produced coatings with average porosity of 12% (APS with PA powder – Fig. 7d) and 17% (APS with HDH powder – Fig. 7g). The microstructure showed interconnected pores, along with small isolated pores. Compared to titanium based coatings produced by APS, FS with PA coating exhibited a much higher porosity percentage in the order of 34% (Fig. 7a) and a higher degree of oxidation. The torch temperature played a significant role in the degree of melting of the particles injected into the jet and consequently, in the final microstructure of the coating. Nelson et al. [14] concluded that Ti-6Al-4V coatings deposited under high temperature, exhibited a more compact, dense and less porous microstructure than that deposited under low temperature. Therefore, a possible justification of the higher porosity of the FS, in contrast to the APS coating, could be the much lower temperature (1500–2000 °C) generated in the torch, comparing to temperatures developed in a conventional plasma jet that range between 8000 and 15,000 °C (maximum of 28,000 °C). This allows the particles to melt in a much more finer lamellae structure, thus filling the space between the coarser particles and form a more dense coating. It should be reminded that both techniques have a deposition efficiency close to 50%, but APS has higher deposition rate (about 80 g/min), in contrast to FS which has a deposition rate of 30–50 g/min. Moreover, the gray interlayer boundaries because of titanium oxidation and other in-flight reactions [22] are pointed by the arrows in Fig. 7b and h. Interconnected porous structure of Coatings 1 and 2 (squares in Fig. 7b and e), is made obvious after detachment of pull-out from the coating and revelation of the coatings inner microstructure (square in Fig. 7e). Isolated pore formation is also pointed out by the arrows in Fig. 7h. The interfaces between the coatings and the substrate were continuous and presented almost no grooves (Fig. 7c and
f). Some voids and a few pores were observed (Fig. 7i) at the interface line, but, being very limited, they are not able to affect the adherence of the titanium coating to the steel substrate.

3.4. X-ray diffraction analysis

The profiles of the coatings that were analyzed with D8 Advance (Bruker Corporation) X-ray diffractometer are presented in Fig. 8a to c. Different crystal microstructures of Ti and peak assignments, were determined for the PA (Fig. 8a and b) and HDH (Fig. 8c) powders that were used as the feedstock material prior to the thermal spray process. Regarding the XRD spectra of the three as-sprayed coatings (Fig. 8a to c), the different phases of Ti are shown in the legend and appear on the diagram with the corresponding colour. The phase analysis shows that after spraying, a roughly estimated 30–40% of the main Ti phase has been transformed to Ti oxide phase in the coatings, though the main Ti phase with hexagonal structure is still existent.

As aforementioned, surface Ti atoms have got oxidized due to heat treatment, in the flame and plasma jets. The distinguished interplanar spacing calculated from reflections makes it possible to identify the following phases in the coatings. In both the coatings of FS and APS with PA powder appear the following oxides; (TiO₀.7₁₆)₃.₇₆ with a cubic lattice and two types of Ti₂O oxides with hexagonal lattice. In the APS coating with HDH powder the two oxides that are present, are TiO₀.₃₂₅ and (TiO₀.₈₉₂)₃.₅₃, exhibiting correspondingly, hexagonal and cubic lattice.

Both the (TiO₀.₇₁₆)₃.₇₆ and (TiO₀.₈₉₂)₃.₅₃ oxides that have been formed in the APS with PA powder and the FS coatings, and in the APS with HDH powder, respectively, have a cubic lattice. This is because, during the thermal spray process, the sprayed powder particles experience high temperatures and melt. Consequently, during the solidification process, depending on the solidification path that is followed by the molten metal and the amount of oxygen that is diffused through the metal, oxides with different lattices are possible to be formed [23].

In conclusion, the powders are composed of hexagonal lattice Ti and the thermal sprayed coatings with both techniques are composed of hexagonal lattice Ti and the aforementioned oxides (Table 4). According to previous study [24], thick titanium oxide layers formed onto a biomedical implant surface can develop a slightly negative surface-charge in a biological environment, which induces electrical attraction to the surrounding ions, such as Ca²⁺. After these ions have accumulated on the implant surface, the surface itself develops a positive charge and begins to further attract negatively charged phosphate ions that react with the calcium ions, in order to form initially amorphous apatite phases. Moreover, it has also been insinuated that the increased wettability of titanium oxide surfaces may be linked to osteoblastic cell attachment and proliferation [25].

3.5. Microhardness

The average and standard deviation values of microhardness of the titanium coatings were obtained by Vickers microhardness test method and are presented in Table 3. All the three coatings present relatively close microhardness values. The coating produced via flame spray process has the lowest mean microhardness value among the coatings and also, the highest standard deviation. This is explained, as the FS-PA
coating contains the greatest total pore volume. Unavoidably, the inhomogeneity factor is introduced to the coating, in contrast to the structural density of the coatings prepared with the APS process. In total, Vickers microhardness of the coatings were found to be elevated in comparison with the average Vickers microhardness 409.8 of commercially pure Titanium – grade 2 [26], due to the presence of titanium oxides in the coatings and at same time in the same order of magnitude with the average Vickers microhardness 866.8 of composite alloy Ti6Al4V [26].

4. Conclusions

Three specimens for each different type of coating were produced by different sets of thermal spray process/feedstock powder (FS with PA powder, APS with PA powder and APS with HDH powder). The porosity of the coatings was investigated, as well as morphology of the surfaces, microstructure and chemical composition. In addition, roughness and thickness data of the coatings were acquired and their biological response in vitro was examined. From the obtained results, it could be concluded that:

- All of the coatings were porous and exhibited heterogeneity in reference with the contained porosity percentages. The average porosity for the FS-PA coating was found to be 34%, for the APS-PA coating 12% and for the APS-HDH coating 17%. Furthermore, only the FS-PA coating enclosk a fraction of pores with an area in the range of 39,000–63,000 μm². Therefore, additional significant cell growth could only be expected in the specific coating.
- All the specimens exhibited a uniform thickness of an average value of 281 ± 20 μm for the FS coating, 239 ± 8 μm for the APS-PA coating and 125 ± 7 μm for the APS-HDH coating. The specimen fabricated by the FS technique was found to be the roughest specimen, with a mean surface roughness (Ra) of 11.19 ± 0.21 μm and also, the most oxidized surface due to its process of fabrication.
- The APS-PA coating presented the greatest density, because the fine spherical particles of the powder feedstock were very well heated and deformed to a very good state of lamellae, so as they filled the spacing between the coarser particles. Careful selection of the spraying parameters and also, the nature of the specific spraying procedure contributed to this outcome.
- XRD analyses of the starting powders, indicated that the principal element present is titanium and that Ti with a hexagonal lattice is the main phase. Following, XRD analyses of the porous titanium coatings revealed the formation of titanium oxides on the coatings after thermal spraying, which may be proven beneficial to the development of osseous tissue.
- Regarding the biological response of the coatings in vitro, it was observed that after immersion of the coatings into the SBF for 7 days, calcium phosphate phases were formed on the surfaces of the coatings, but did not cover them completely. These calcium phosphates were mostly agglomerated particles that consisted of spheroid globules with typical size of about 1 μm or less. Ca/P ratio was found to be very different to that of stoichiometric hydroxyapatite, probably due to short residence time of the specimens.

![Optical micrograph of the cross section of (a) FS-PA coating, (d) APS-PA coating and (g) APS-HDH coating. SEM micrograph of the cross section of (b) FS-PA coating, (e) APS-PA coating and (h) APS-HDH coating. SEM micrographs (c) on etched AISI 304 stainless steel substrate, (f), (i) of the interface between the pure titanium coatings and the substrate.](https://example.com/image)
into the SBF. After 14 days of immersion spheroid globules of less than 0.5 μm in size were spotted on the surfaces of the coatings and the Ca/P ratio on the FS-PA coating was 1.61, which denotes the presence of a biphasic calcium phosphate. Although the calcium phosphate particles did not form a coherent layer onto the titanium surfaces, their dispersion all over the surfaces is an initial example of the presence of a biphasic calcium phosphate. Although all the coatings are characterized by adequate porosity percentage, the FS-PA coating presents the possibility for additional significant cell growth and thus future satisfying anchoring of the implant.

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