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# Microstructural comparison of the surfaces of Ti-6AL-4V and Ti-6Al-7Nb alloys with $TiO_2$ deposition by plasma spray

## Comparação microestrutural das superfícies das ligas Ti-6AL-4V e Ti-6Al-7Nb com deposição de $TiO_2$ por plasma spray

## Comparación microestructural de las superficies de las aleaciones Ti-6AL-4V y Ti-6Al-7Nb con deposición de $TiO_2$ por pulverización de plasma

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**Abstract**

Metallic biomaterials in the oral cavity exposed to extreme conditions that affect it and reduce its biofunctionality. Surface modification by plasma spray oxide deposition is one of the methods used as an alternative to improve the bioactivity of Ti alloy implants. The objective of this work was to study the physicochemical surface characteristics of Ti-6Al-4V and Ti-6Al-7Nb alloys modified by $TiO_2$ coating via plasma spray and thermochemical treatment with NaOH. The Ti-6Al-4V and Ti-6Al-7Nb alloys obtained in a cylindrical shape, sectioned in the longitudinal direction, and sectioned with dimensions of 20 mm in diameter and 2 mm in thickness, sanded and polished. The microstructure revealed using Kroll's solution. Then, titanium oxide ($TiO_2$) powder deposition performed on Ti-6Al-4V and Ti-6Al-7Nb samples and submitted to thermochemical treatment with NaOH solution. The physical-chemical characterizations and elemental analysis performed using argon-induced plasma emission spectrometry (ICP), X-ray fluorescein spectrometry (XRF), scanning electron microscopy (SEM), X-ray diffraction (XRD). The results showed a rough and porous $TiO_2$ coating morphology. $TiO_2$ deposition resulted in an apparent mixture of stoichiometric and non-stoichiometric oxides on the substrate surface, in addition to presenting an optimization in the substrate/coating interaction with the NaOH treatment, leading to an increase in the surface area. It seen that the $TiO_2$/Ti-6Al-4V/ and $TiO_2$/Ti-6Al-7Nb systems present good chemical adhesion between substrate and coating, and the layer formed by the $TiO_2$ coating associated with the treatment with NaOH presents a relevant level of porosity, being an important feature for osseointegration.

**Keywords:** Ti-6AL-4V alloy, Ti-6Al-7Nb alloy, Surface treatment, NaOH.

**Resumo**

Biomateriais metálicos na cavidade oral expostos a condições extremas que a afetam e reduzem sua biofuncionalidade. A modificação da superfície por deposição de óxido por plasma spray é um dos métodos utilizados como alternativa para melhorar a bioatividade de implantes de ligas de Ti. O objetivo deste trabalho foi estudar as características físico-químicas superficiais das ligas Ti-6Al-4V e Ti-6Al-7Nb modificadas por revestimento de $TiO_2$ via plasma spray e tratamento termoquímico com NaOH. As ligas Ti-6Al-4V e Ti-6Al-7Nb obtidas em forma cilíndrica, seccionadas no sentido longitudinal, e seccionadas com dimensões de 20 mm de diâmetro e 2 mm de espessura, lixadas e polidas. A microestrutura revelada usando a solução de Kroll. Em seguida, foi realizada a deposição de pó de óxido de titânio ($TiO_2$) em amostras de Ti-6Al-4V e Ti-6Al-7Nb e submetidas a tratamento termoquímico com solução de NaOH. As caracterizações físico-químicas e análise elementar foram realizadas por meio de espectrometria de emissão de plasma induzido por argônio (ICP), espectrometria de fluoresceína de raios-X

(XRF), microscopia eletrônica de varredura (MEV), difração de raios-X (DRX). Os resultados mostraram uma morfologia de revestimento de $TiO_2$ rugoso e poroso. A deposição de $TiO_2$ resultou em uma aparente mistura de óxidos estequiométricos e não estequiométricos na superfície do substrato, além de apresentar uma otimização na interação substrato/revestimento com o tratamento com NaOH, levando a um aumento da área superficial. Verificou-se que os sistemas $TiO_2$/Ti-6Al-4V/ e $TiO_2$/Ti-6Al-7Nb apresentam boa adesão química entre substrato e revestimento, e a camada formada pelo revestimento de $TiO_2$ associado ao tratamento com NaOH apresenta um nível de porosidade relevante, sendo uma característica importante para a osseointegração.
**Palavras-chave:** Liga Ti-6AL-4V, Liga Ti-6Al-7Nb, Tratamento de superfície, NaOH.

**Resumen**
Biomateriales metálicos en la cavidad bucal expuestos a condiciones extremas que la afectan y reducen su biofuncionalidad. La modificación de la superficie mediante la deposición de óxido por pulverización de plasma es uno de los métodos utilizados como alternativa para mejorar la bioactividad de los implantes de aleación de Ti. El objetivo de este trabajo fue estudiar las características fisicoquímicas superficiales de las aleaciones Ti-6Al-4V y Ti-6Al-7Nb modificadas por recubrimiento de $TiO_2$ vía plasma spray y tratamiento termoquímico con NaOH. Las aleaciones Ti-6Al-4V y Ti-6Al-7Nb obtenidas en forma cilíndrica, seccionadas en sentido longitudinal, y seccionadas con dimensiones de 20 mm de diámetro y 2 mm de espesor, lijadas y pulidas. La microestructura revelada utilizando la solución de Kroll. Luego, se realizó la deposición de polvo de óxido de titanio ($TiO_2$) en muestras de Ti-6Al-4V y Ti-6Al-7Nb y se sometieron a tratamiento termoquímico con solución de NaOH. Las caracterizaciones físico-químicas y el análisis elemental se realizaron mediante espectrometría de emisión de plasma inducida por argón (ICP), espectrometría de fluoresceína de rayos X (XRF), microscopía electrónica de barrido (SEM), difracción de rayos X (XRD). Los resultados mostraron una morfología de recubrimiento de $TiO_2$ rugosa y porosa. La deposición de $TiO_2$ resultó en una aparente mezcla de óxidos estequiométricos y no estequiométricos en la superficie del sustrato, además de presentar una optimización en la interacción sustrato/revestimiento con el tratamiento con NaOH, lo que llevó a un aumento en el área superficial. Se observó que los sistemas $TiO_2$/Ti-6Al-4V/ y $TiO_2$/Ti-6Al-7Nb presentan buena adherencia química entre sustrato y recubrimiento, y la capa formada por el recubrimiento de $TiO_2$ asociado al tratamiento con NaOH presenta un nivel de porosidad relevante, siendo una característica importante para la osteointegración.
**Palabras clave:** Aleación Ti-6AL-4V, Aleación Ti-6Al-7Nb, Tratamiento superficial, NaOH.

## 1. Introduction

Titanium and its alloys have excellent biocompatibility, due to good corrosion resistance in physiological fluids and acceptable tissue tolerance. The initial phase of contact (titanium/tissue) is associated with the interaction of a biological fluid, blood, spittle, or extracellular fluids, producing the adsorption of macromolecules from the fluid on the surface of the implant.(Kuroda et al., 2020; Niinomi et al., 2014; Yeung et al., 2013) In this process, proteins are present, where adsorption plays a crucial role in the biocompatibility mechanism, being linked to the direct interactions produced at the interface. (Cooper, 2000; Khan et al., 1999; Manam et al., 2017; Mohammed et al., 2015)

The presence of the oxide layer, mainly $TiO_2$, on the surface of titanium and its alloys plays a very important role in the favorable tissue response to the implant.(Albrektsson et al., 1987; Casaletto et al., 2001; Manjaiah & Laubscher, 2017) $TiO_2$ has attractive properties, which include high hardness, high refractive index, great chemical stability, making $TiO_2$ crystalline coatings of great interest in important applications in the fields of chemical engineering, in addition to being widely studied as a coating for biomaterials for presenting good bicompatibility, since the biocompatibility and osseointegration of the titanium implant is associated with a thin oxide layer that spontaneously forms on the material's surface. (Albrektsson et al., 1987; Casaletto et al., 2001; Manjaiah & Laubscher, 2017)

To create a new surface with different properties when compared to uncoated devices, some studies have attempted to modify the surface using $TiO_2$ deposition, as according to some authors, the chemical surface modification of cp Ti and its alloys with deposited a layer of $TiO_2$, increases the surface area and, consequently, the anchorage power to the bone, facilitating osseointegration. (Boyd et al., 2008; Montanha, 2010)

Titanium oxide coating can obtain using different deposition techniques, in this work the technique of choice was the plasma spray process as it is a versatile technique and provides a coating with a rough and porous morphology, as well as the choice of parameters used. for the deposition of $TiO_2$ (Alencar, 2002) aiming to study the physical and chemical characteristics of the surface of Ti-6Al-4V and Ti-6Al-7Nb alloys modified by $TiO_2$ deposit via plasma spray and thermochemical treatment with NaOH.

## 2. Material and Methods

The commercial alloy Ti-6Al-4V ELI (BALMER) and Ti-6Al-7Nb (SANDINOX), in cylindrical shape sectioned in the longitudinal direction with the aid of a precision cutting disc model 15 HC DIAMOND in an ISOMET cutting machine 1000 – BÜEHLER, to obtain samples with dimensions of 20 mm in diameter and 2 mm in thickness. Afterwards, the mechanical polishing conducted using water sandpaper with a granulation of 400 to 1000 mesh, the polishing was done with a damp cloth and an aqueous suspension of 1.0 and 0.3 µm alumina. To reveal the microstructures, the Kroll reagent used: 1HF 85% /1$HNO_3$ 65%/100 $H_2O$ (v/v) and chemical attack times between 1 to 10 minutes.

The specimens of the Ti-6Al-4V and Ti-6Al-7Nb alloys subjected to a cleaning process with acetone, to eliminate organic impurities. Then, commercial titanium oxide powder ($TiO_2$) METCO 102 (BRASTAK Ltda) deposited on the alloys under study.

$TiO_2$ depositions conducted in the Plasma-Spray Gun equipment – Metco Perkin Elmer, in which the samples of Ti-6Al-4V and Ti-6Al-7Nb fixed on a support at 100 mm from the torch. The coatings subjected to working conditions, using a current of 500 A, voltage of 65 V and a speed in the range of 1 to 2 Mach (the speed of the deposited ion can be about twice the speed of sound, where 1 Mach=340 m/s). The specimens of the alloys with $TiO_2$ deposit were subjected to treatment in a NaOH solution (5.0 mol. $L^{-1}$) for 24 hours at 60°C. After this treatment, they were oven dried for 3 hours at 60°C.

The titanium oxide powder and the coated Ti-6Al-4V and Ti-6Al-7Nb specimens were characterized using the following techniques: Argon Induced Plasma Emission Spectrometry (ICP) by an Atom Scan Atomic Emission Spectrometer 25 - Thermo Jarrel Ash and C and S Elementary Analyzer, CS-444 - LECO, X-ray diffraction (DRX) with a SIEMENS D5000 diffractometer, with angular scanning between 10° and 50º, in Bragg-Brentano assembly using Cu radiation (kα1) and Rigaku X-ray diffractometer, model D/MAX System – 2100/PC, using copper $K_\alpha$ radiation (1.5405A) with Ni filter for $K_\beta$ radiation with an ULTIMA theta-theta goniometer with a speed of 2 degrees $min^{-1}$ being the accelerated copper $K_\alpha$ radiation source with a potential of 40kV and a current of 20 mĂ and angular scanning between 10° and 50°, in the Bragg-Brentano assembly , scanning electron microscopy (SEM) using a LEO microscope, model 440 coupled to an X-ray energy dispersive scattering spectroscopy (EDS) analyzer and Si(Li) elemental mapping with Be window, model 760 and resolution of 133eV energy dispersive spectroscopic – EDS, in addition to X-ray fluorescence spectrometry (XRF) by an Energy Dispersive X-Ray Fluorescence spectrometer (EDX-800 RayNy), brand Shimadzu, which in this case has an XRF energy system dispersive EDS

## 3. Results

Table 1 presents the results obtained for the titanium oxide powder and coating, where distinct amounts of oxygen and titanium detected and different from the nominal composition. Suggesting that this difference in relation to the starting material is due to the thermal decomposition of the $TiO_2$ powder. Considering that the temperature at the gun outlet can reach 1500°C, the titanium dioxide powder will undergo atomic dissociation, which will later recombine on the surface with other elements present in the substrates. In plasma, the atomization process of constituents, interaction and formation of compounds are very fast, not allowing thermodynamic equilibrium to be established, and the following reactions may occur. (Alencar, 2002)

$$2TiO_2 \xrightarrow{plasma} 2Ti + 2O \rightarrow Ti_2O_3 + Ti_{substrate} + O \rightarrow 2TiO_2$$

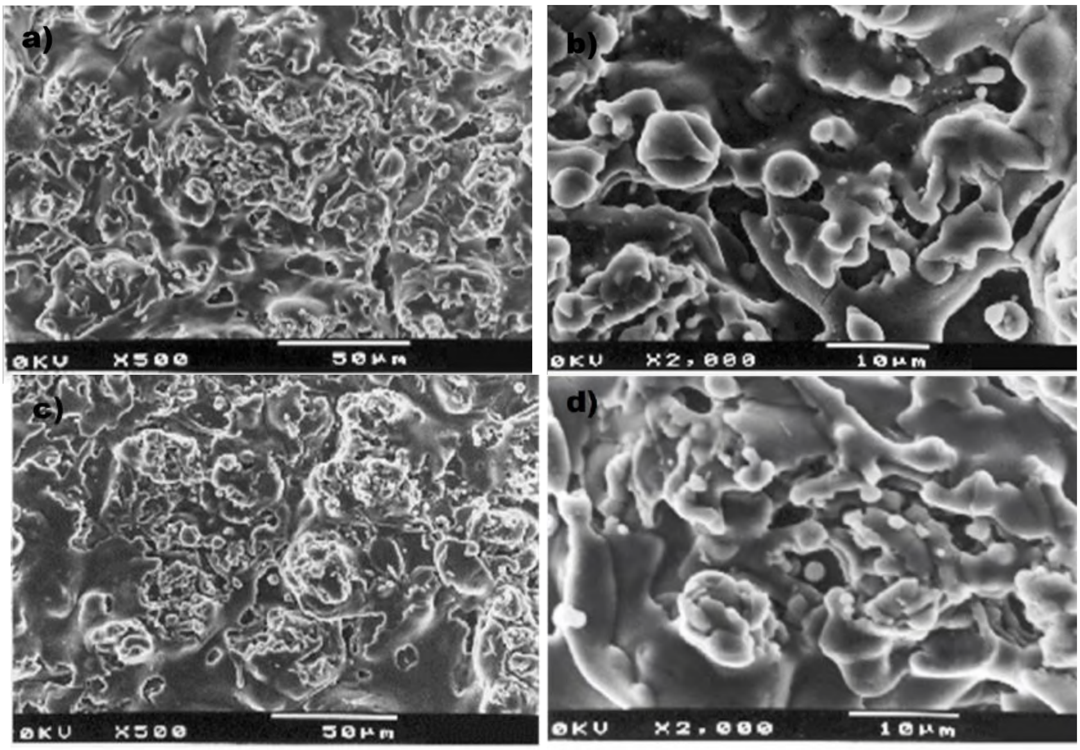
**Table 1**. Chemical composition of the $TiO_2$ coating (%m/m).

| Elements (% máx) | Nominal Composition (%) | $TiO_2$ powder | Coating |
|---|---|---|---|
| O | 40 | 25.13 | 19.54 |
| N | - | 1.663 | 0.01098 |
| Ti | 60 | Balance | Balance |

Source: Survey data.

Figure 1 shows the micrographs obtained by scanning electron microscopy of the surface of the $TiO_2$ coating on the Ti-6Al-4V and Ti-6Al-7Nb alloys. Figures 1a and 1b represent the Ti-6Al-4V alloy, where a morphology with high roughness and greater thickness can be seen, in addition to observing in Figure 1b a characteristic surface of the coatings made by the plasma-spray technique.(Fauchais PL, Heberlein JVR, 2014; Minati et al., 2017) These coatings are made in the form of several layers, with a lamellar aspect, and are composed of molten particles, partially molten and some voids between the deposited layers. The morphology of the deposit is very rough and porous. (De Almeida Filho et al., 2007; Fauchais PL, Heberlein JVR, 2014) Figures 1c and 1d represent the Ti-6Al-7Nb alloy where characteristics like those of the Ti-6Al-4V alloy observed. In $TiO_2$ coatings small cracks observed, which according to the literature generated by residual stresses resulting from the thermal effect.

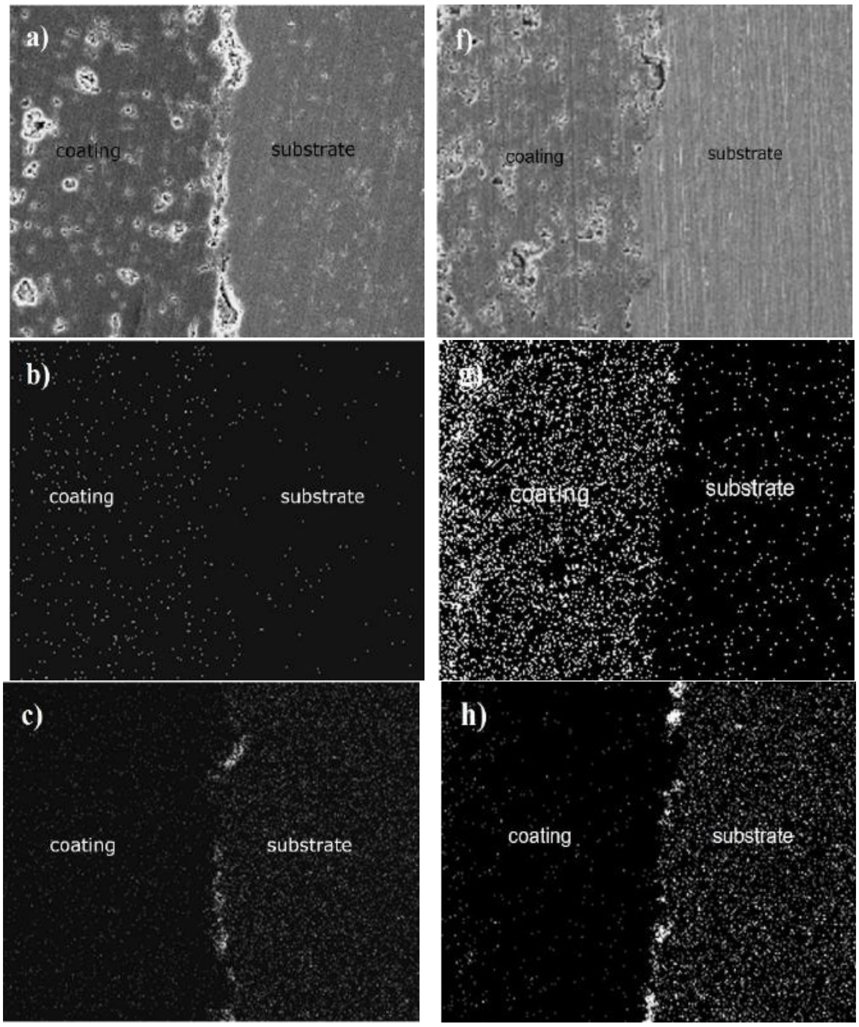
**Figure 1**. Micrographs of $TiO_2$ coating on Ti-6Al-4V (a, b) and Ti-6Al-7Nb (c, d) alloys.

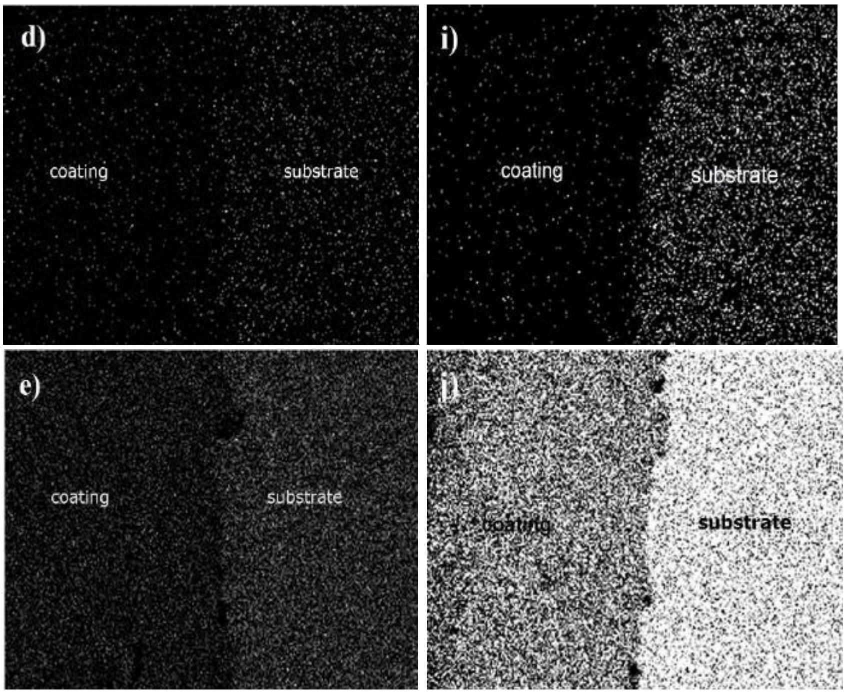



Source: Survey data.

Figure 2 shows the $TiO_2$ /Ti-6Al-4V and $TiO_2$ /Ti-6Al-7Nb interface elementary mapping using SEM/EDS. Figure 2a shows the region of the substrate/coating section for the Ti-6Al-4V alloy where the mappings of the Ti, Al, V and O elements performed. The same occurs in Figure 2f, where the elements Ti, Al, Nb and O were mapped. In Figure 2b, which corresponds to the oxygen mapping (bright spots) for the Ti-6Al-4V alloy, and in Figure 2g, the mapping of oxygen for the Ti-6Al-7Nb alloy, it is observed that the amount of oxygen detected in the coating is much greater than that of the substrate in both alloys, which can probably be related to the existence of several oxides that make up the coting. In the mapping done for aluminum, Figure 2c, for the Ti-6Al-4V alloy and Figure 2h, for the Ti-6Al-7Nb alloy, presents a greater amount in the substrate, which already expected because this metal is part of the composition from both leagues. In Figure 2d, for the Ti-6Al-4V alloy, it can observe in the vanadium mapping the existence of a large amount of vanadium in the deposit, this occurred during the sample preparation, which sanded and polished, which may have the element present in the substrate has dragged into the deposit. As in Figure 2i, for the Ti-6Al-7Nb alloy, the niobium mapping observed. The mapping performed for titanium, shown in Figure 2e, for the Ti-6Al-4V alloy and Figure 2j, for the Ti-6Al-7Nb alloy, also shows a greater amount of the element in the substrate than in the coating, as expected.

**Figure 2**. Substrate/coating cross section mapping for alloys: $TiO_2$ /Ti-6Al-4V, (a) photo mapped region, (b) oxygen mapping, (c) aluminum mapping, (d) mapping of the vanadium and (e) titanium and $TiO_2$ /Ti-6Al-7Nb mapping, (f) photo mapped region, (g) oxygen mapping, (h) aluminum mapping, (i) niobium mapping and (j) mapping of titanium. Increase: 1000X.

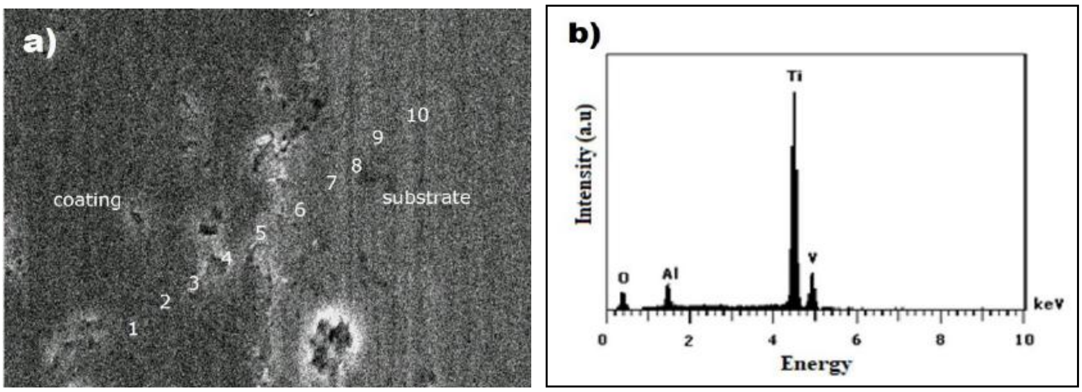





Source: Survey data.

Figure 3a shows the semi-quantitative spot chemical analysis at the deposit/substrate interface of the Ti-6Al-4V alloy. This analysis performed at ten different points within a 50µm range (represented by the numbers 1 to 10). Figure 3b shows the result of an analysis performed by EDS at point 10 of the sample, where the presence of Ti, Al and V related to the composition of the substrate observed.

**Figure 3**. (a) Spot analysis of the coating/substrate interface for Ti-6Al-4V. 1000X magnification. (b) Analysis of Ti-6Al-4V alloy substrate by EDS.




Source: Survey data.

Table 2 shows the results of the microanalysis with the concentrations of oxygen, aluminum, vanadium, and titanium at each point. It observed that the closer to the substrate region, the detected amounts of vanadium and aluminum increase (point 5). Another interesting fact is the amount of oxygen found in the substrate region (point 6), which may be associated with the diffusion of oxygen from the coating to the interior of the substrate. This diffusion is possible because in the plasma state dissociations occur in $TiO_2$ atoms and as the substrate reaches a high temperature there may be a "fused" surface layer where oxygen diffusion occurs, which can be considered as the occurrence of a strong interaction between the substrate and the coating since there is inter-diffusion between them. (De Almeida Filho et al., 2007)

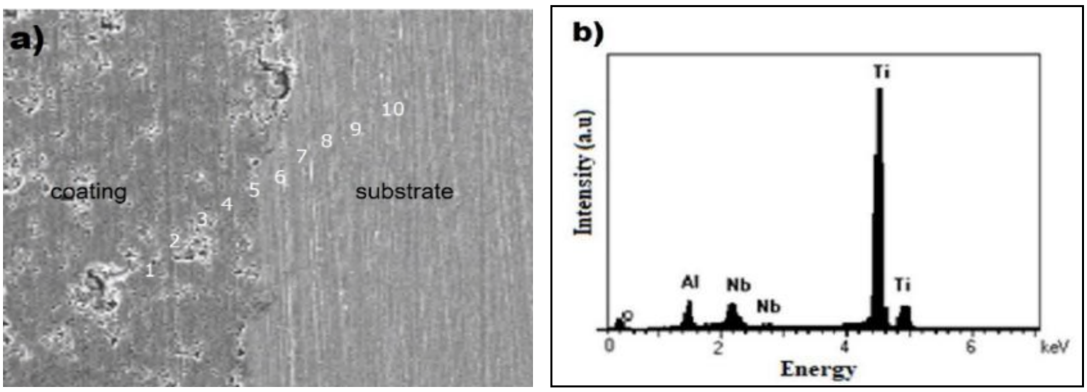
**Table 2.** EDS microanalysis results for Ti-6Al-4V (%m/m).

| | | Elements | | | |
|---|---|---|---|---|---|
| | Spots | Ti | Al | V | O |
| Coating | 1 | 38.9 | 0.2* | 0.5* | 60.2 |
| | 2 | 60.3 | 0.1* | 0.7* | 38.9 |
| | 3 | 43.6 | 0.1* | 0.5* | 55.7 |
| | 4 | 51.4 | 0.2* | 0.3* | 47.8 |
| Interface | 5 | 56.3 | 5.8 | 2.6 | 35.2 |
| Substrate | 6 | 71.5 | 5.2 | 2.3 | 20.9 |
| | 7 | 75.9 | 4.7 | 3.1 | 16.2 |
| | 8 | 77.1 | 4.8 | 3.4 | 14.7 |
| | 9 | 72.8 | 4.8 | 2.9 | 19.6 |
| | 10 | 7.2 | 4.8 | 3.5 | 14.5 |

* the values found are close to the equipment's margin of error, and the error equals ± 0.1 of the atomic percentage of the element.
Source: Survey data.

Figure 4a shows the region where the semi-quantitative punctual chemical analysis performed at the coating/substrate interface of the Ti-6Al-7Nb alloy. This analysis performed at ten different points within a 50μm range (represented by the numbers 1 to 10). Figure 4b shows the results obtained by EDS performed at point 10 of the sample. It observed the presence of Ti, Al, Nb and O referring to the alloy composition in the substrate region.

**Figure 4**. (a) Spot analysis of the coating/substrate interface for Ti-6Al-7Nb. 1000X magnification, (b) Analysis of Ti-6Al-7Nb alloy substrate by EDS.




Source: Survey data.

The results of the microanalysis with the concentrations of oxygen, aluminum, niobium, and titanium at each spot presented, Table 3. It can observe the amount of oxygen significantly decreases at spot 6 but there is diffusion of oxygen from the coating to the interior of the substrate. The non-quantification of the element niobium and aluminum in the region of the coating may be related to their quantities being smaller than the minimum detected by the equipment, although their presence in the coating not expected.

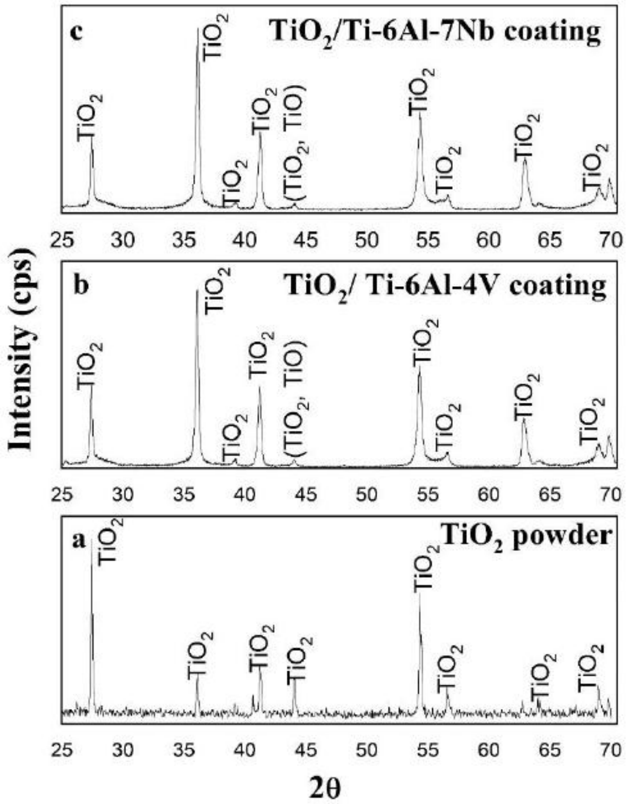
**Table 3.** EDS microanalysis results for Ti-6Al-7Nb (%m/m).

| | Spots | Elements Ti | Al | Nb | O |
|---|---|---|---|---|---|
| Coating | 1 | 70.0 | - | - | 29.9 |
| | 2 | 66.0 | - | - | 33.9 |
| | 3 | 64.9 | - | - | 35.1 |
| | 4 | 59.4 | - | - | 40.6 |
| Interface | 5 | 65.4 | - | - | 34.6 |
| Substrate | 6 | 80.4 | 8.2 | 4.2 | 7.2 |
| | 7 | 86.9 | 3.9 | 5.5 | 3.6 |
| | 8 | 87.8 | 5.2 | 4.1 | 2.8 |
| | 9 | 83.6 | 3.6 | 10.3 | 2.4 |
| | 10 | 84.0 | 3.9 | 8.9 | 2.5 |

Source: Survey data.

Figure 5 shows the diffractograms obtained from the $TiO_2$ powder, used as starting material, and from the coating conducted on the substrates Ti-6Al-4V and Ti-6Al-7Nb. It observed in Figure 5a, only the diffraction lines of the rutile phase of $TiO_2$ (n.86-0147) in the starting powder observed, confirming the information obtained from the supplier of the starting material. In the plasma-spray coating diffractogram, Figure 5 (b and c), the diffraction lines referring to the rutile phase of $TiO_2$ (n.86-0147) and TiO (n.85-2084) (JCPDS, 2003) were identified thus, showing the difference in composition between the starting material and the coating.

**Figure 5.** X-ray diffractograms (a) $TiO_2$ powder (b) $TiO_2$ / Ti-6Al-4V coating (c) $TiO_2$ / Ti-6Al-7Nb coating.




Source: Survey data.

Although the $TiO_2$ deposited substrate is more favorable, a mixture of stoichiometric and non-stoichiometric oxides, less thermodynamically stable on the surface may be present. Figure 6 (a, c), shows a porous morphology and irregular lamellae, not juxtaposed, on the surface of the $TiO_2$ deposited on the Ti-6Al-4V and Ti-6Al-7Nb alloys, treated with a NaOH solution, Figure 6 (b, d), to increase surface activity, which suggests better nucleation of calcium phosphate derivatives. The treatment of the surface of $TiO_2$ deposited by plasma-spray with NaOH showed a fibrous structure of sodium titanate (He et al., 2016), as in the treatment carried out directly on the surface of the alloys.

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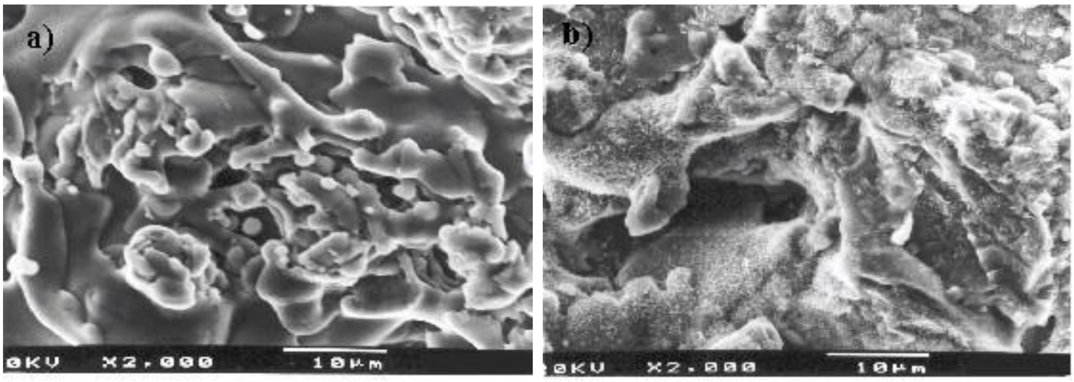
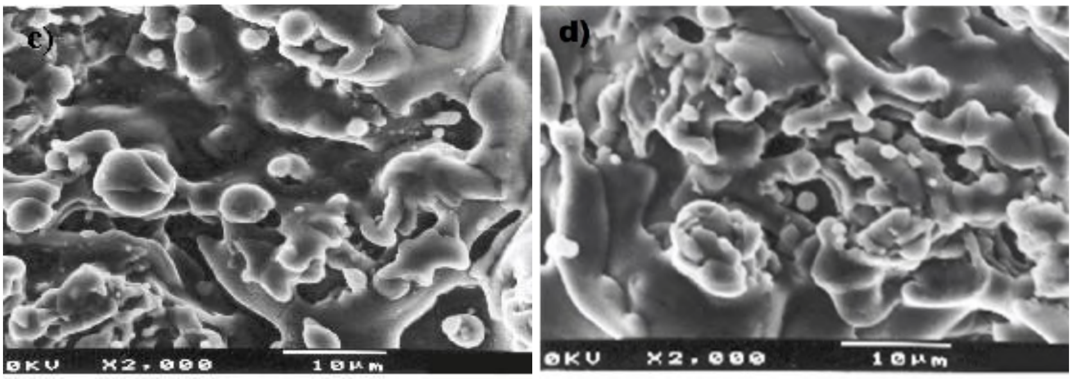
**Figure 6.** Micrographs of the surface of the $TiO_2$ coating on Ti-6Al-4V and Ti-6Al-7Nb (a, c) before and (b, d) after thermochemical treatment with the NaOH solution.

**$TiO_2$/ Ti-6Al-4V**



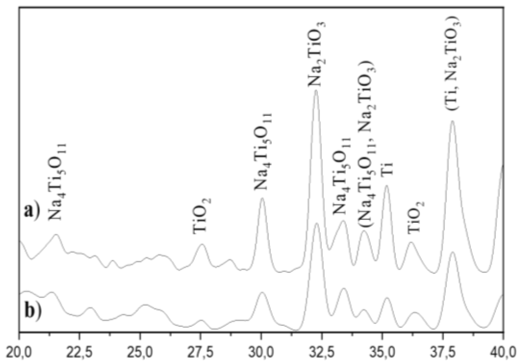

**$TiO_2$ / Ti-6Al-7Nb**




Source: Survey data.

Figure 7 corresponds to an X-ray diffractogram of both alloys, where it is possible to confirm the formation of the sodium titanate layer, after thermochemical treatment.

**Figure 7**. X-ray diffractograms (a) $TiO_2$/Ti-6Al-7Nb (b) $TiO_2$/Ti-6Al-4V after treatment with NaOH.




Source: Survey data.

## 4. Discussion

The plasma-spray process reaches very high temperatures (~20,000°C), but the cooling time of a particle is in the order of 10-7 to 10-6 seconds.(Fauchais PL, Heberlein JVR, 2014; M.J. Kadhim, M.H. Hafiz, 2017; Minati et al., 2017) How each particle reaches the substrate after 0.1 s of the arrival of another particle has arrived, 106 times the cooling time of the particle, it is concluded that the heat transfer process of a particle is not influenced by the other. A study carried out by Zaat demonstrated there is a relationship between thermal conductivity and heat capacity that describes how the particles and the substrate gain, lose and transfer heat.(M.J. Kadhim, M.H. Hafiz, 2017) This relationship proves that the substrate melts only if it is deposited by plasma-spray refractory metals (Mo, W, Ta, Nb). The physicochemical modification of the substrate surface through this $TiO_2$ deposit presented a structure composed of a mixture of stoichiometric and non-stoichiometric oxides with different thermodynamic stabilities (different enthalpies), increased the anchoring power and improved the interaction with $Ca^{2+}$ ions and $PO_4^{3-}$.

Studies highlight important effects of surface modification and increased roughness in the bone/implant interaction, such as: improved fixation of cells to the implant surface, increased presence of bone on the implant surface, increased biomechanical interaction of the implant with the bone. (Cooper, 2000)

## 5. Conclusion

From the results obtained, it could conclude:

- Plasma spray deposition of $TiO_2$ is an efficient method for surface modification when it intended to increase the interaction of ions and improve the biomechanics of the biomaterial.

- The temperature of the plasma spray deposition process has a strong influence on the growth, crystallization, and morphology of the oxide films.

- Surface modification with $TiO_2$ via plasma-spray process associated with thermochemical treatment with NaOH in Ti-6Al-4V and Ti-6Al-7Nb alloys, optimized and directly influenced the substrate/coating interaction, providing a strongly adhered, highly porous coating, rough and with lamellae.

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