

**Scratch-resistant and well-adhered nanotube arrays produced via anodizing process
on β -titanium alloy**

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Abstract

Well-adhered nanotube arrays were produced through the anodizing technique on a Ti-25Nb-25Ta alloy and tribo-mechanically evaluated by nanoindentation and nanoscratch tests. Disregarding substrate effects, the hardness of the nanotube arrays layer was 0.7 ± 0.1 GPa and elastic modulus was < 12 GPa, respectively. With the load increase and nanotubes compaction, hardness reached 1.8 GPa and elastic modulus stabilized in ~ 40 GPa, which features a mechanically biocompatible gradient zone for implant applications. Under scratching, plastic deformations predominated in the nanotube arrays coating, which mechanism was load-dependent: in the first stage (up to 50 mN) and the initial tubes collapsing, the coating presented low cohesive strength; under higher loads and the progressive nanotubes compaction, the cohesive strength increased, as suggested by the pattern of cracks produced. The scratch resistance for the coating failure was higher than 500 mN, consisting of an excellent bonding adhesion for a nanotube layer produced by anodization.

Keywords: β -Titanium alloys; Ti-25Nb-25Ta; nanotube; anodizing; nanoscratch; nanoindentation.

1 Introduction

Nanotubes are nanometric scale tubular structures, which can be formed in self-ordered arrays in a preferred direction [1,2]. TiO₂ nanotubes have been considered for a wide range of applications as photocatalysis [3], biosensors [4], solar cells [5] and biomaterials [6]. The nanotube arrays can be formed through processes as the sol-gel technique, hydrothermal treatments, and anodizing [1,2]. The anodizing (also called anodic oxidation) is an efficient method to produce highly ordered nanotube arrays coatings on valve metals like titanium (Ti), niobium (Nb) and tantalum (Ta) [7,8].

All these metals present good biocompatibility, non-toxicity and excellent corrosion resistance [9,10]. Such properties are related to the high chemical affinity of the valve metals with oxygen, which forms a protective barrier that keeps the metal isolated from the biological environment [10]. By alloying Ti, Nb, and Ta, one obtains the Ti-25Nb-25Ta alloy, which presents elastic modulus much lower than standard metallic materials (like pure Ti and Ti6Al4V) employed in orthopedic implants [11–13]. Lower elastic moduli values, closer to the bone tissue values, are more adequate for application in orthopedic devices to avoid the stress shielding effect. The matching elastic modulus promotes better distribution of loads between the implant and bone, avoiding a possible lack of mechanical stability caused by the reduction of bone density (osteopenia) in the implant/bone interface [14]. However, the elastic modulus of Ti-25Nb-25Ta alloy (~70 GPa) is still higher than that of bones (10-40 GPa). A possible solution to decrease bone resorption is to introduce a mechanical accommodation zone in the bone/metal interface, which is expected to function as a mechanical adapter. Porous oxide, such as nanotube arrays, can play the role of the mechanical adapter.

Due to the dimensions of the nanotubes and the nanotube array, suitable techniques of mechanical properties measurements must be selected. The nanoindentation is an efficient technique to obtain qualitative and quantitative measurements of mechanical properties in thin films and coatings, and it has been also applied on nanotube arrays [15–18]. When the nanoindentation is performed in a conventional mode, the test evaluates the mechanical features of the nanotube array in its axial growth direction. The scratch-resistance of the layer is evaluated by adding a tangential force to the normal mode of indentation [16,19–22]. Typically, the nanoscratch test consists of applying a crescent force during the tip sliding against the layer; the coating performance is evaluated through the critical load for which adhesion fails [15].

For a wide range of applications, the nanotube arrays must present improved tribo-mechanical properties and the increase of adhesion strength is directly related to the increase of the coating durability [23]. However, nanotube arrays obtained by anodization process frequently present a poor adhesion in the metal/coating interface [24]. Furthermore, there is a large field to be explored in this area and a need for better comprehension of nanoscratch tests on nanotube arrays produced via anodic oxidation. [17]. Thus, the objectives of this work were to produce a well-adhered coating of nanotube arrays on the promising Ti-25Nb-25Ta alloy for application on biomaterial area and to evaluate its mechanical and tribological properties through the nanoindentation and nanoscratch tests.

2 Experimental procedure

2.1 Specimen preparation

The samples were prepared from the Ti-25Nb-25Ta alloy. The alloy was made by melting pure Ti (99.8% purity), Nb (99.7% purity), and Ta (99.8% purity) in an electric arc furnace in an atmosphere of argon gas. The metal percentage in weight was 50% of Ti, 25% of Nb, and 25% of Ta. The produced alloy was submitted to two heat treatments:

1st- Low gradient of cooling temperature - The alloy temperature was increased up to 950 °C and after was slowly decreased (~24 h of cooling)

2nd- High gradient of cooling temperature - The alloy temperature was increased up to 850 °C and submitted to 1 h of cooling.

The specimens were cut from the alloy ingots, sanded, polished using colloidal silica (0.3 μm - particle diameter), and ultrasonically cleaned in acetone, ethanol, and distilled water (15 min in each solvent).

2.2 Anodizing conditions

The anodizing was carried out at room temperature, under constant stirring, in an acrylic electrolytic cell, applying 60 V constant voltage (potentiostatic mode) for 1 hour. The electrolyte employed consisted of ethylene glycol C₂H₄(OH)₂ + 5% (wt.) of deionized water + 0.5%(wt.) of ammonium fluoride. The experimental parameters chosen for this work represent the best condition found among a wide range of different experimental settings tested in a master thesis (see reference [25]). The voltage and the electrolyte are a variation based on previous work conducted by Tang *et al* on titanium [26].

2.3 Characterizations

After anodic oxidations, the morphologies were observed using a TESCAN VEGA3 LMU Scanning Electron Microscope (SEM). This facility is equipped with an EDS (Energy Dispersive X-Ray Spectroscopy) analyzer, which allowed the study of the chemical composition of the surfaces.

To obtain an average inner diameter of the nanotubes, measurements using the ImageJ software were carried out from the top view, coincident with the growth orientation and measurements of the external diameter were obtained through cross-sectional SEM images. They were made more than 100 measurements of the diameters in 3 different oxide regions.

A UNAT Nanoindenter (Zwick-Roell/Asmec) was employed to evaluate the mechanical properties of the nanotube array layers, by applying the *Quasi Continuous Stiffness Measurement* procedure. 49 indentations were made with a spherical tip (radius = 5 μm) under 500 mN maximum load. In this method, depth-dependent hardness and elastic modulus values can be calculated during the indentation process, which provides several points profile. Besides, more accurate values can be found under very small forces (< 0.5mN) and the time of measuring is faster than that for cyclic measurements.

The nanoscratch tests were performed in the same nanoindentation facility and the same spherical tip running a scratch length of 300 μm and applying an increasing load up to 500 mN, i.e., the loading rate was 1.67 mN/ μm . Typically, they are performed on coatings of 0.1-20 μm thick 3 to 5 scratches per sample [27]. In this study, 5 scratches were performed and analyzed. After the scratch test, line EDS

analyses were performed along the formed grooves to detect if and where the oxide was completely removed to associate to a critical load.

3 Results and Discussion

3.1 Morphology

The nanotube morphologies obtained by the anodization process are shown in Fig. 1. The nanotube arrays presented a good area distribution with minor variations in the tube's shape and diameter.

To obtain an average inner diameter of the nanotubes, measurements were carried out from the top view, coincident with the growth orientation; measurements of the external diameter were obtained through cross-sectional SEM images, as can be seen in Fig. 2a and Fig. 2b, respectively. The nanotubes grown on the Ti-25Nb-25Ta alloy presented an internal diameter of 57 ± 2 nm and an external diameter of 170 ± 2 nm.

Along with the tubular structure, the layer also presented nano and micrometric pores generated by the pitting phenomenon – they are better seen under lower SEM magnifications and they appear indicated by yellow arrows in Fig. 3.b (also, pores can be seen following the text in Fig. 5.a, Fig 6.a and Fig 7.a,b). The presence of nano and micrometric pores may be a good combination for biomaterial devices where osseointegration is required. Micrometric porous structures are associated with a faster healing process than non-porous surfaces [28]. Moreover, bone grows inside micrometric pores [29], which improves implant mechanical stability. On the other hand, nanostructures have a better interaction with cells and proteins [30]. It also displayed an influence on adhesion, proliferation, differentiation of cells [31], and a

faster apatite formation than micrometric pores (when soaked in Simulate Body Fluid - SBF) [32].

3.2 Nanoindentation

The chosen nanoindenter tip was the spherical one, which is more suitable than sharp indenters to evaluate nanotube arrays [17]. The sphere diameter (10 μm) is large as compared to the tube one (88 nm), allowing that several tubes can be deformed together; moreover, the contact area under the spherical indenter is much higher than that under usual pyramidal tips, which results in lower pressures and better control of deformations during the test. After each indentation, the nanotubes arrays were plastically deformed forming semi-spherical imprints. An image of an indentation imprint can be seen in Fig 3 b. The semi-spherical shape indicates that the surface was orthogonal in relation to the load applied by the nanoindenter tip. For the maximum 500 mN axial force, no cracks or pile-up effect (which could affect the measured values) were detected at the edges of the imprint [15]. In the mechanical measurement processes obtained by indentation techniques, the contact area is an important parameter. In the nanoindentation case, the contact area is obtained differently. Knowing the tip geometry, the area is calculated as a function of tip penetration [15]. That is, the indentation must be done following an orthogonal orientation concerning the surface to avoid affecting the indirect area measurement and, consequently, the mechanical properties measurements [15].

Nanoindentation is a suitable technique for measuring mechanical properties of micrometer-thick thin layers on substrates. However, both substrate and coating react together to the mechanical *stimulus*, so the final result contains information of the

whole system; besides, the substrate contribution increases with the penetration depth of indentation. However, if the coating thickness is known, it is possible to estimate the effective mechanical properties of the coating in separated. For *hardness*, such estimation is made in penetrations up to 10% the coating thickness to minimize the substrate influence, since up to this depth the plastic stress field is constrained inside the layer [15]. The coating thickness was $12 \pm 1 \mu\text{m}$, measured from 10 different sites of cross-sectional SEM images, as shown in Fig 3a. These are relatively high-length nanotubes, a result that can be attributed to the type of electrolyte employed in the anodization process [8].

As seen in Fig. 4, the indentation tests were limited to depths inside the nanotubes array layer, not reaching the interface. The right side of the gray area in Fig. 4.a represents the 10% limit of the indenter penetration depth. Even in this region, hardness values varied significantly with depth, from 0.2 to 0.7 GPa. Under low loads and low pressures produced at the beginning of indentation, the contact was Hertzian with purely elastic deformations, as verified in the loading curves (not shown); plastic deformations took place as the load increased. Hence, by considering the presence of effective plastic strains and the substrate influence, the value obtained at the limit of 10% penetration depth can be assumed as the most representative of the nanotubes array layer: $0.7 \pm 0.1 \text{ GPa}$. As the depth increased, hardness increased continuously as well, now also influenced by the Ti-25Nb-25Ta substrate, which hardness was 1.8 GPa. There is a clear discontinuity present in the profile at the tip penetration depth $1.9 \mu\text{m}$ and the corresponding load of 50 mN (as indicated by arrows in Fig.4), where hardness suddenly increased. This abrupt change in mechanical behavior is believed to be caused by a collapse of a high number of nanotube units followed by its densification,

as seen in Fig. 3.b. Even though the unique tubular layer morphology demanded spherical tips for its characterization, it must be stressed that hardness measured with this kind of indenter is possibly underestimated: the maximum shear stresses responsible for plastic strains are not right in the tip-surface contact, but at a depth corresponding to 0.5 the tip radius, i.e., in a region with higher substrate influence [15].

Differently from hardness, the 10% penetration depth rule is not suitable for elastic modulus, since elastic stress fields propagate much deeper in the material than the plastic ones. Effective elastic modulus, independent of the substrate, demand more complex analyses that can be tricky and inaccurate for this uncommon structured coating [16]. Because the substrate influence is depth-dependent and, unlike pyramidal tips, loss of geometric shape at shallow depths is less important in spherical indenters, elastic modulus measured with the latter geometry under low loads can be assumed as being representative figures for the layer behavior. Hence, the elastic modulus of the nanotube arrays layer was <12 GPa, corresponding to the shallowest depth in Fig. 4.b. As expected, this value is much below the one for bulk TiO_2 (~250 GPa [33]), which reflects the strong effect of the tubular structure on the material properties.

The profile increased with depth due to the substrate influence; for comparison purposes, the elastic modulus of the Ti-25Nb-25Ta substrate is approximately 70 GPa [34]. However, elastic modulus values remained practically constant at a lower value, ~40 GPa, after 3 μm depth and the discontinuity point. This effect can be attributed to the extreme change in morphology experienced by the layer during indentation, as

nanotubes are crushed and compacted (see Fig. 3.b). Even if the original microstructure was lost, such an amorphized layer can have a beneficial effect on biocompatibility. As stated in Section 1, elastic moduli values close to the bone values (10-30 GPa [10]) are more adequate for applications in orthopedic devices to avoid the stress shielding effect [14]. The nanotubes array layer, even if severely deformed, can act as a mechanical accommodation zone in the bone/metal interface with the function of a mechanical adapter, so avoiding the abrupt elastic moduli mismatch. As the mechanical solicitation increases, the elastic modulus of the layer changes up to a maximum value that is still intermediate between bone and Ti-25Nb-25Ta.

Of course, the effectiveness of such an elastic moduli gradient through the compacted layer depends on the layer stability on the surface. The adhesion of the nanotube arrays is analyzed in the next section.

3.3 Nanoscratch

Fig.5 displays one of the five scratches performed on the anodized surface with the respective line scan EDS profiles (the yellow line corresponds to the exact location of the EDS analysis). It is important to emphasize that the line covered by the EDS (475 μm) is greater than the length of the scratch (300 μm). It is possible to observe the material pile-up on the groove edges (mainly at the scratch's end) and some launched particles remained close to the groove. EDS did not detect any sudden increase of the Ti percentage, which means the increasing force applied was not enough to expose the metallic substrate. Thus, the critical force to expose the substrate was > 500 mN.

The three curves in Fig. 5b represent profiles of the groove in three different stages of the nanoscratch test. The first curve (black line) corresponds to a previous

scanning made under low force (0.2 mN) to get the original profile without damaging the surface. The second curve (red) was recorded during the force application, while the third one (grey) corresponds to the groove produced by the applied force. The profile during scratch (red curve) and after scratch (red curve) are different due to the elastic behavior of the coating. Therefore, the gap between the red and grey curves represents the elastic recovery after the scratch process. Up to 30 μm (50 mN normal force), there was an overlap of the grey and the red curves, i.e., there was only plastic deformation. For loads higher than 50 mN elastic recovery also took place, however, with the predominance of plastic deformation. It is worthwhile recalling that, in nanoindentation tests (Fig. 4), hardness and elastic modulus profiles also presented an abrupt change under 50 mN applied load. Scratch tests differ from indentation tests by involving both normal and tangential forces; as a result, plastic deformations are constrained in regions surrounding the sliding tip [15]. Despite the different regimes, it is possible to assume that 50 mN correspond to a threshold load up to which the nanotubes undergo an initial plastic-dominant strain, possibly featured by the tubes collapsing. Higher loads contribute to the compaction and amorphization of the material. The nature of such plastic deformation under low loads will be discussed further.

Fig. 6-a shows details of the groove portion where the applied load had a range of 0 – 55 mN (at the beginning of the scratch test), and Fig 6-b,c displays a higher magnification of the groove that was made by a load of ~ 30 mN. The image shows deformed areas, cracks spread from the groove to the outside scratch region, and regions with relatively small spalled areas producing "step formation" on the groove. The tubular structure was partially preserved in this region, as shown in the insets.

Hence, cracks on the layer were produced under low normal and lateral forces. It shows a poor cohesive strength between the nanotubes nearby the surface. For larger loads (250 mN up to 500 mN), as shown in Fig. 7, there was neither complete removal of the coating nor spalling of blocks from the coating, but the nanotube arrays were amorphized. Besides, according to the scratch atlas [35], there was a pattern of almost orthogonal cracks (striated) to the direction of the groove that resembles the shape of conformal and arc tensile cracks.

Fig. 8 is a sketch for explaining the nanoscratch process on the nanotube array. When the tip starts to penetrate and slide, it produces compressive stresses (in front of the indenter tip) and tensile stresses (back of the indenter tip) [23] on the nanotube coating. In response to the compressive stress, nanotubes deform plastically and elastically. In response to the tensile stress, cracks are formed to release stress after exceeding the fracture toughness limit.

From the middle to the end of the scratch groove, the tip applies a higher load onto the nanotube coating, which causes flexion, collapse, and the compaction process (densification) of the nanotubes at the region under compressive stress. The compacted region also forms cracks under tensile stress. According to Bull's study, cohesive failure for ductile and brittle coating substrates present tensile and Hertzian cracks that can evolve into adhesive failures such as chipping and spallation processes [36]. However, no adhesive failures were observed in the oxide/alloy interface, which suggests a good bond between the substrate and the anodic coating [37] (since the substrate was not exposed). Another remark is that, typically in scratch tests with increasing load, firstly chevron cracks (cohesive failure pattern in the coating) are

observed. As the load increases the failures change to the arc tensile cracks pattern, and finally evolve to chipping failure (adhesive failure) [35].

The failures observed in the nanotube coating, as previously discussed, are presented in a different sequence. As the mechanical properties change abruptly at the 50 mN applied force, we could consider a modification to a different oxide configuration after this force. The change to the new configuration is evidenced by the coating behavior in the narrow load range before 50 mN / after 50mN. Thus, the "step formation" (chipping failure) formed by applying low loads would be analogous to an adhesive failure at the oxide configuration below 50 mN in relation to the oxide coating configuration after 50mN, despite being a cohesive failure. Briefly, the scratch test only produced a cohesive failure in the coating and the coating showed signs of excellent adhesion with the substrate.

Table 1 presents a comparison of nanoscratch tests carried out with other oxide surfaces obtained by anodizing (nanotube arrays) and by Plasma Electrolytic Oxidation (PEO). Nanotube arrays, in general, show poor adhesion to the substrate [24], while oxide coatings formed by PEO are known to present good adhesion [23]. It is also important to remark that experimental parameters influence the adhesive failure results, especially the tip geometry used during the nanoscratch measurements. For instance, damages produced by pyramidal tips are more severe than with round tips. When the nanotube arrays coatings are compared with PEO coatings, generally PEO coatings present significantly greater adhesive failure force, which can be 114 times greater. When a similar comparison using the spherical tip is done, the adhesive failure can be up to 27 times.

Among the works cited in Table 1, there is a recent study that produced a Two-Step PEO coating on the Ti-25Nb-25Ta alloy [22]. The coating was evaluated similarly as in the present study, using the same equipment, scratch distance, same spherical tip, but a lower maximum force (300 mN). The substrate demonstrated an adhesive failure to a normal force of 275 mN. Here, a 500 mN maximum normal force was employed with no adhesive failure observed, that is, the adhesive failure is > 500 mN and can be approximately 2 times greater than for the surface produced by Two-Step PEO in the same alloy. Additionally, it is possible to observe that the nanotube arrays produced in this work can reach a critical load performance 50 times higher than the nanotube arrays mentioned in table 1. Thus, the present nanotube arrays coating was the most resistant in scratch tests, among all those cited in Table 1.

Nanotube arrays obtained by the anodization process frequently present poor adhesion in the metal/coating interface as shown in table 1, and this issue limits its application in applied surface science because the increase of adhesion strength is directly related to the increase of the coating durability. If the coating durability is guaranteed, the nanotube arrays coating can play the role of a mechanical/biological adapter of the implant. Therefore, the nanotube arrays coating produced in this work can be used to better the mechanical and biological interactions of the implant and the osseous tissue.

5 Conclusion

Well-adhered nanotube arrays coating was obtained by the anodizing process on the Ti-25Nb-25Ta alloy. The coating formed presented the following characteristics:

- The nanotubes grew aligned to the normal vector of the alloy surface and showed a low variation of dimensions, which presented an internal diameter of 57 ± 2 nm, an external diameter of 170 ± 2 nm and a length of 12 ± 1 μ m.
- The estimated hardness and elastic modulus values of the layer were 0.7 ± 0.1 GPa and > 12 GPa, respectively. The hardness and elastic modulus profiles increased with depth, presenting a discontinuity at 50 mN applied force, which is suggested to be due to the nanotubes collapsing. Above the discontinuity, the hardness increases sharply reaching 1.8 ± 0.1 GPa at deeper regions inside the coating (corresponding to the maximum load of 500 mN), while the elastic modulus remained constant in about 40 GPa, which is a lower value than the substrate.
- The layer disclosed distinct mechanical behaviors marked by the transition at 50 mN normal load for scratching and indentation test. Up to this limit, there was undetected elastic recovery, and after it, plastic deformations predominated. For shallow depths and low forces (< 50 mN), the coating presented low cohesive strength, however, under higher loads, the pattern of cracks suggested a good cohesive strength. Moreover, for the employed 500 mN maximum load, adhesive failure was not observed. In comparison with other studies from literature, it is possible to assume an excellent bonding adhesion in the coating/alloy interface.

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List of Figure captions

Figure 1. SEM image of the nanotubes grown on Ti-25Nb-25Ta alloy. The magnifications used were a) 30 kx and b) 60 kx. It's possible to see only minor variations in the shape and diameter of the nanotubes.

Figure 2. Top view with measurements of the inner diameter (a) and cross-sectional view with outer diameters (b) of the nanotubes, obtained by SEM.

Figure 3. a) cross-sectional SEM image of the nanotube arrays layer with the respective coating thickness and b) SEM image of an imprint made by nanoindentation on the top surface, normally to the tube growth direction. The tiny pores seen in (b) are the nanotubes opening to the surface (indicated by yellow arrows).

Figure 4. Hardness (a) and Elastic modulus (b) as a function of tip normal displacement obtained by nanoindentation. The grey area represents 10% of the coating thickness and the force (50mN) is related to a point that shows an abrupt change in mechanical behavior, possibly due to a collapse of a large number of nanotubes.

Figure 5. A typical groove of a nanoscratch test performed on the nanotube's arrays layer. a) Line scan EDS made onto the scratch grooves. The yellow horizontal line represents the exact region where the chemical composition was taken. The black curve represents the titanium atomic percentage at the respective line. b) profile

curves obtained before (black curve), during (red curve), and after (gray curve) the nanoscratch test.

Figure 6. SEM image at the beginning of the groove produced by the nanoscratch process (low normal loads- 0 -55 mN) with magnifications of a) 5kx b) 20kx, and c) 50kx. The center of the yellow square corresponds to a normal load of 33 mN.

Figure 7. SEM image of the middle (250 mN) a) and of the end (500 mN) b) of a typical groove produced by the nanoscratch process, with a magnification of 5 kx.

Figure 8. Scheme of the nanoscratch process on the nanotube array using a spherical tip under increasing load.

Table 1. Comparison of studies regarding adhesive failure made by nanoscratch tests on nanotube arrays and PEO coatings.

Substrate	treatment	Electrolyte – electrical parameters – time	Maximum load (mN)	Tip	Adhesive failure-force (mN)
Niobium [21]	Two-step PEO	P electrolyte: 1 mol·L ⁻¹ H ₃ PO ₄ (80 vol.%) + 35% H ₂ O ₂ . Ca electrolyte: 0.5 mol·L ⁻¹ Ca(CH ₃ CO ₂) ₂ ·H ₂ O 1 st step: P electrolyte - 30 s - 200V. 2 nd step: P (25% vol.) + Ca (75% vol.) - 60 s – 350V	400	Berkovich	>400
Niobium [21]	Two-step PEO	1 st step: P electrolyte - 30 s - 200V. 2 nd step: P (50% vol.) + Ca (50% vol.) - 60 s – 350V	400	Berkovich	266.7
Niobium [38]	PEO	P electrolyte - 60 s -350V.	400	Berkovich	280
Niobium [38]	PEO	Ca electrolyte - 60 s -170V.	400	Berkovich	50
Niobium [38]	PEO	P (50% vol.) + Ca (50% vol.) - 60 s – 350V	400	Berkovich	220
Sandblasted titanium [39]	PEO	A1 electrolyte: 0.14 mol L ⁻¹ Ca(CH ₃ CO ₂) ₂ ·H ₂ O + 0.06 mol. L ⁻¹ of sodium biphosphate dihydrate -100s - 150 mA/cm ²	400	Berkovich	> 400
Titanium [39]	PEO	A1 electrolyte – 100s - 150mA/cm ²	400	Berkovich	135
Ti-25Nb-25Ta [22]	Two-step PEO	1 st step: P electrolyte - 30 s - 300V. 2 nd step: P (20% vol.) + Ca (80% vol.) - 60 s – 350V	300	Spherical (5 μm-radius)	275
Ti-25Nb-25Ta (this work)	Anodizing – nanotube matrix	ethylene glycol C ₂ H ₄ (OH) ₂ + 5% (wt.) of deionized water + 0.5%(wt.) of ammonium fluoride – 1 hour-60 V	500	Spherical (5 μm-radius)	>500
Ti-25Nb-25Ta [25]	Anodizing – nanotube matrix	H ₃ PO ₄ + 0.8%wt. of NH ₄ F - 3 hours- 25 V	500	Spherical (5 μm-radius)	162
Titanium [25]	Anodizing – nanotube matrix	H ₃ PO ₄ + 0.8%wt. of NH ₄ F - 1 hour - 25 V	250	Spherical (5 μm-radius)	< 10
Titanium [40]	Anodizing – nanotube matrix	H ₃ PO ₄ + 0.3 %wt. of HF - 1 hour - 15 V	50	Spherical (75 μm-radius)	< 10
Titanium and Ti Alloys [41]	Anodizing – nanotube matrix	0.5wt% of NaF+ 2.7wt% of Na ₂ SO ₄ 20 min – 25V Heat-treated: 450°C for 3 h	20	Berkovich	< 10

