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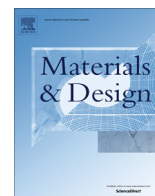
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Functionalization of Ti6Al4V scaffolds produced by direct metal laser for biomedical applications



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ABSTRACT

Direct metal laser sintering (DMLS) is a powerful tool to produce titanium based biomaterials because the ease to convert 3D medical imaging data into solid objects with excellent mechanical and corrosion properties. DMLS samples can be functionalized by anodizing, allowing the growth of titanium oxide layers of enhanced properties. In the present paper, a complete characterization of the microstructure, mechanical properties and particularly, the corrosion behavior has been carried out to assess their possible use as biomaterial. The results of the anodized scaffolds are very promising, showing a Young Modulus near to the cortical bone and a low corrosion rate, ensuring their suitability for medical applications.

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1. Introduction

In less than three decades and more especially since 2007, additive manufacturing (AM) has emerged as a significant driving force in advanced manufacturing [1]. This process, also known as solid freeform fabrication (SFF) or three-dimensional (3D) printing has been defined by ASTM as “a process of joining materials to make objects from 3D model data, usually layer upon layer, as opposed to subtractive manufacturing methodologies” [2].

There are several processes for additive manufacturing and new market niches that make them very attractive to the industry [3–5]. The use of directed energy beams and especially lasers has enabled producers to move from prototypes and casting inserts at best to manufacture end-use parts with complex shapes that can be useful in automotive, aerospace, or biomedical industries. Particularly, for the fabrication of medical prosthesis the industry is becoming very active because of the ease in which 3D medical imaging data can be converted into solid objects [6,7].

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Laser additive manufacturing (LAM) also known as laser sintering (usually referred to polymers), laser melting or direct metal laser sintering (DMLS) is a very attractive technique because of the high production rates, savings in tools and materials, the complexity of the shapes that can be designed and the excellent mechanical and corrosion properties that can be achieved. Despite its recent development, there is abundant literature on the use of DMLS for processing different metallic materials from light alloys to superalloys, covering a broad range of applications. Literature is being enhanced significantly for DMLS new uses and materials, from new light alloys [8] to stainless steels [9], titanium alloys [10] or special applications as the processing of Fe-bulk amorphous alloy coatings [11]. DMLS would be particularly relevant to produce complex solid structures and porous components of titanium and titanium alloys to be used directly as metallic biomaterials. Jardim et al. [12] have recently used the additive manufacturing technique to create an anatomic biomodel of a bone for surgical planning.

Just like other biomaterials, DMLS biomaterials need to present good mechanical and corrosion properties, high wear resistance as well as to improve bioactivity and osseointegration of the metal implant. However, as Kurella and Dahotre [13] clearly expressed

“it is rare to find a material that meets all the requirements of a given application, and biomaterials are no exception”. Therefore, the engineered scaffolds take biodegradability, cell biology, biomolecules and material mechanical properties into account [14]. Such a highly complex and demanding system, needs the optimization of the surface properties of biomaterials. It is generally accepted that the use of surface modification techniques will allow tailoring the surface characteristics in order to enhance its bioactivity and physicochemical properties.

Among the different surface treatments available for titanium alloys, anodizing allows the growth of titanium oxide layers under controlled conditions [15,16]. Both, the structure and composition of the anodic layer can be controlled by varying the electrolyte composition, the applied voltage, time and temperature [17,18]. In general, anodic oxide layers grown on titanium and its alloys in acidic HF-containing electrolytes exhibit duplex structure comprising by an outer nanoporous/nanotubular layer in contact with the electrolyte, and an inner compact layer (barrier layer) at the bottom of the nanotube/nanopore adjacent to the substrate [19–21]. This technique has been widely used to fabricate TiO₂ nanotubes with different properties such as dye-sensitization [22], controlled wettability [23], photocatalytic [24] or biomedical [25,26] but a few papers deals with the anodization of materials produced by Direct Metal Laser Sintering [27,28]. Therefore, the objective of this paper is to produce DMLS specimens of Ti6Al4V alloy and its surface modification by electrochemical oxidation with a particular focus on the corrosion properties of the functionalized alloy surface.

2. Experimental

The specimens used for this investigation were produced by DMLS technique using EOSINT M 270 machine from EOS GmbH Electro Optical Systems, equipped with a 200 W single mode Ytterbium fiber laser at 1070 nm wavelength from IPG Photonics. In DMLS technique, the powder is spread and processed by the action of the laser in an inert and thermally controlled environment inside a chamber. A system of scanning mirrors controls and drives the laser beam describing the geometry of the layer on the surface of the spread material. With the incidence of the laser, the particles of material are heated and reach its melting point, joining each other and also to the previous layer. When the material solidifies, a new powder layer is added over the sintered layer and the laser scans the desired areas once more, in other words, after the sintering of a layer, a new layer is deposited, and this process goes on until the construction of the part is finished. Thus, the solid model is built layer by layer [29,30].

The laser beam was focused to a spot size of 50 μm diameter and a power of 170 W on the building platform. Pre-alloy powders of Ti6Al4V alloy (EOS Titanium Ti64) were used to fabricate the scaffolds. This powder had spherical morphology with an average particle size of 50 μm (Fig. 1), as determined by a LEO 440i scanning electron microscope. The processing parameters used to manufacture the specimens were scan speed of 1250 mm/s, hatch spacing of 100 μm and layer thickness of 30 μm . The same scanning strategy was applied to manufacturing all specimens. An alternating scanning vector was used and the scanning direction was rotated 45° to each successive layer. The processing was carried out under argon shielding gas (argon grade 4.8, purity 99.998%, O₂ < 5 ppm) to monitor the oxygen level within the chamber, acting also as protective gas.

The specimens were designed as solid disks of 10 mm diameter and 4 mm thickness and scaffolds of the same dimensions, Fig. 2. The scaffolds showed regularly arranged pores interconnected

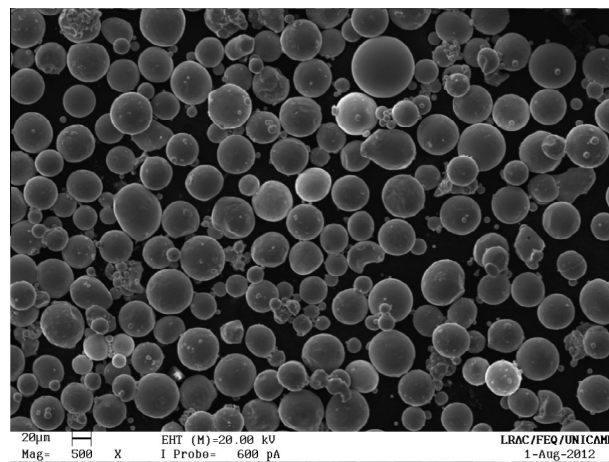


Fig. 1. SEM micrograph of the spherical powder with an average particle size of 50 μm .

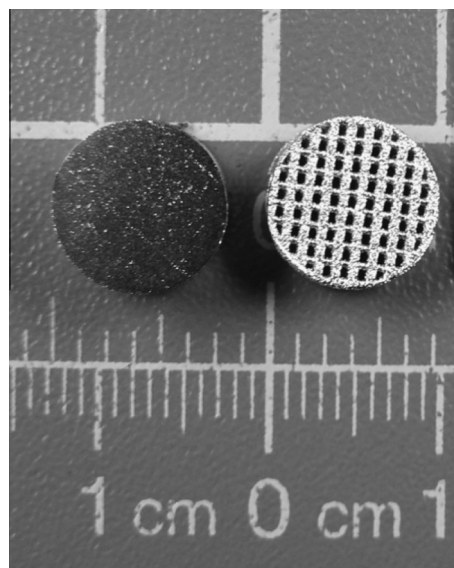


Fig. 2. DMLS samples of Ti6Al4V. Left, solid specimen, right, scaffold.

three dimensionally. The unit cell is in the form of a prism with a strut dimension of $510 \pm 50 \mu\text{m}$ by $500 \pm 50 \mu\text{m}$.

Once the specimens were processed, they were chemically polished in a mixture of HF(40 wt.%):HNO₃(70 wt.%):H₂O with volume ratio 1:4:5 for 5 min at room temperature under continuous agitation at 400 rpm, rinsed in distilled water and dried in cold air.

The mechanical properties of Ti6Al4V alloy were conducted by a micro-hardness tester (Nanotest 600 from Micromaterials) equipped with a Berkovich type indenter, using a load of 500 mN and performing nine indents for each specimen to obtain average values of the Young's modulus and hardness. Vickers micro-hardness measurements, with a load of 10 N during 15 s (HV_{0.1}), were also carried out using a Wilson Wolpert micro-hardness tester.

X-ray diffraction (XRD) measurements were carried out on solid DMLS specimens in a Bruker AXS D8 Advance diffractometer equipped with central Euler ring and scanner in X–Y with monochromatic Co K α radiation ($\lambda = 1.789010 \text{ \AA}$). Diffraction data were collected in the angular range 20° to 125° 2 θ with a step-size of 0.02° and 2 s of counting time.

Anodic films were fabricated in a two-electrode cell by anodizing the specimens at constant voltage at 20 V in the electrolyte containing 1M H₂SO₄ and 34.5 mM HF for 5 min at constant temperature at 20 °C. Platinum plate was used as cathode. The chemical composition, morphology and properties of these surfaces have been described elsewhere [31,32].

The morphology of the porous anodic oxide layers was examined by field emission gun scanning electron microscopy (FEG-SEM) utilizing a JSM6500F JEOL instrument equipped with EDX facilities.

The corrosion behavior of both type of materials before and after anodizing were characterized by electrochemical measurements in phosphate buffered saline solution (PBS) with a pH value of 7.2–7.4 prepared from the analytical reagents and deionized water. The electrochemical measurements were carried out using a three-electrode cell connected to a Gamry Reference 600 Potentiostat. The specimens were used as working electrode, a platinum wire as an auxiliary electrode, and a Silver–Silver chloride electrode (Ag–AgCl) as a reference electrode. The electrolyte cell was maintained at 37 ± 2 °C throughout the test. The anodic polarization curves were measured from –0.3 V (vs. Ag–AgCl) to +3 V (vs. Ag–AgCl) with a scan rate of 0.16 mV/s after immersed the specimen into the aggressive electrolyte for 3600 s.

Roughness measurements were performed using a confocal profilometer Sensofar Plμ2300 using an optical objective 20xEPi. The linear measurements were performed over distance of 635 μm in X axis and 476 μm in Y axis. The estimation of Ra was obtained using the standard ASME B.461 using a cut-off length of 0.080 mm ($\lambda_c = 0.08$ mm).

3. Results and discussion

3.1. Microstructural and compositional characterization

After processing, the DMLS specimens presented a different surface appearance depending on the final shape. Although both specimens, solid and scaffolds, had a high roughness, solid specimens were more uniform than the scaffolds, Fig. 3a and b. In both cases but especially in the latter, it can be seen the presence of powder grains stuck on the surface. Such heterogeneous surface leads to a misleading roughness estimation. In order to functionalize the surfaces, both types of specimens were chemically polished in the HF/HNO₃/H₂O acid solution for 5 min. After chemical etching, most of the attached particles have been removed from the surface (Fig. 3c and d). Therefore, the average roughness decreased drastically, being in the range of 500 nm for the solid specimens (zones free of pores) and 2.642 μm ± 1.2 μm for the scaffolds (measured along the strut in both vertical and horizontal directions). In the scaffolds, there are still some particles attached to the inner pore walls by a neck.

The difference in the surface roughness observed between the solid specimens and the scaffolds are due to the different processing procedure. In solid specimens, the laser beam melts all the powder to build a fully dense material. However, for cellular solids or scaffolds, DLSM results in uncontrolled and inhomogeneous powder grain deposition on the beam surfaces, making necessary to develop complementary strategies for preparing the surface for future use [33]. Chemical etching presents several advantages (cheap, quick and highly selective among others) for the post-processing of DLSM specimens. Pyka et al. [34] have stressed the importance of an acid etching for an effective removal of the attached particles although they have also reported some reduction of the mechanical properties on scaffolds as a consequence of increasing the pore size and a decrease in the strut thickness.

Fig. 4 shows the microstructure of the Ti6Al4V processed by DLSM obtained at the longitudinal cross section and the transverse cross section (Fig. 4a and b). The solid and scaffold samples showed a similar grain structure. The picture shows a martensitic microstructure, mainly fine needles like acicular α/α' phase with a very fine phase dispersed throughout the matrix, presumably β -phase. In Fig. 5a, can be seen a magnification of this β -phase and, for comparison purposes, the microstructure of a Ti6Al4V alloy ELI grade (Fig. 5b) according to the standard ASTM F136-02 has been included in the figure. As is pictured, there is a remarkable reduction in β -phase size from the micrometer to the nanometer scale. This can be explained in terms of the relatively fast cooling due to the high solidification rates of laser processing, which leads to the formation of the finer α -phase and retention of the high temperature β -phase at room temperature. So, the transformation of β – α during solidification would be restricted as it has been also pointed out by Balla et al. [35]. Fig. 6 shows the X-ray diffractograms of the Ti6Al4V ELI grade and the solid specimen. As it can be observed, there is no evidence of β -phase in the specimens processed by laser, due to the nanometric size of this phase promoted by the processing conditions. Similarly, it cannot be distinguished if it is α or α' phase because they have the same crystalline structure and then the diffractogram will show the same pattern. In a previous paper, some of the authors have found similar results in specimens processed in the same way [36].

3.2. Mechanical properties

In relation with mechanical properties, the hardness and reduced elastic modulus (E_r) of the solid specimens is related to the Young modulus of the tested specimens following the Eq. (1):

$$\frac{1}{E_r} = \frac{1 - \nu^2}{E} - \frac{1 - \nu_i^2}{E_i} \quad (1)$$

The measurements were performed using a Berkovich diamond tip with Young modulus (E_i) and Poisson coefficient (ν_i) of 1141 GPa and 0.07 respectively.

The hardness of the solid specimen was 4.15 ± 0.31 GPa. The Vickers micro-hardness was found to be 364.1 ± 4 HV which is in the same range of that measured by microindentation.

The Young modulus estimated was of 119.53 ± 3.16 GPa which is in the same order of magnitude to that reported in the literature for Ti6Al4V alloy obtained using a conventional processing method [37]. However, Young's modulus of Ti6Al4V is about 3–10 times higher than that of bone (10–30 GPa). This mismatch of modulus between the metallic implant and surrounding bone tissue can lead to the known as “stress shielding”. It avoids a good fixation of implantation materials to the bone tissue [38] producing the bone resorption and consequently leading to mechanical failure of the implant and even to biological infection.

A new strategy for reducing stress shielding is to use porous metallic alloys because the introduction of porosity into titanium alloys may significantly decrease the Young modulus in relation with bulk material [39,40]. Bandyopadhyay et al. [41] using the laser engineered net shaping, a similar technique to DMLS, obtained porous specimens with a porosity ranging about 23–32% with E comprised between 7 and 60 GPa. More recently, Lin et al. [42] have produced by DLSM titanium specimens of Ti6Al4V for dental implants with elastic modulus of 35 GPa, which are really close to the cortical bone. On the other hand, Rubinstein et al. [43] sintered spongy titanium granules getting values of the elastic modulus as low as 3.5 GPa which are close to those of trabecular bone tissue. In all cases, porosity plays an important role for determining the mechanical properties. There is a general agreement that for porous elastic materials, the relationship

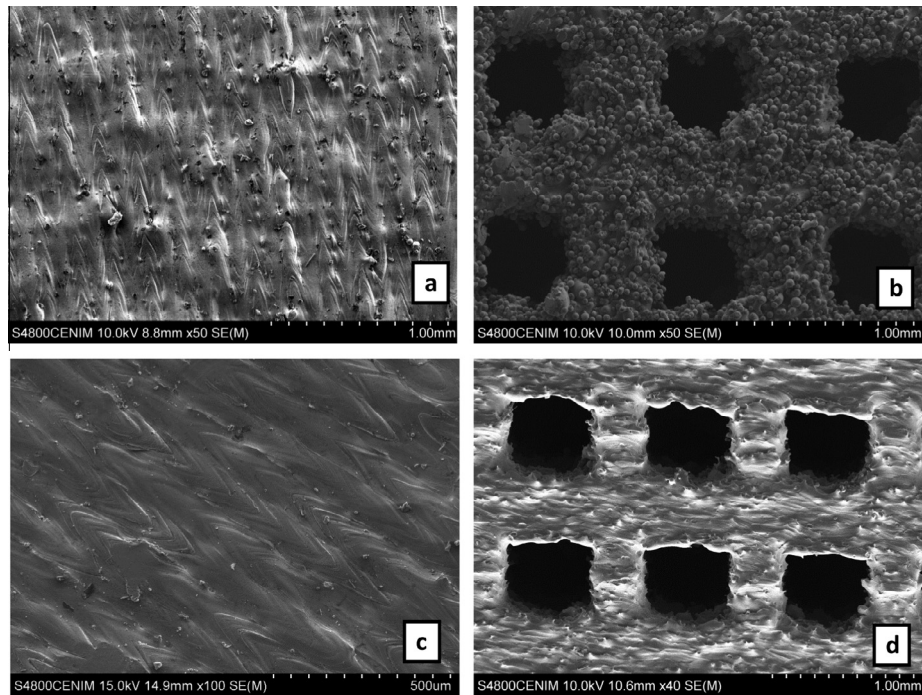


Fig. 3. Samples before and after chemical polishing. (a and b) Solid and Scaffold samples as processed and (c and d) solid and Scaffold specimens after chemical etching in HF/HNO₃ acid solution for 5 min.

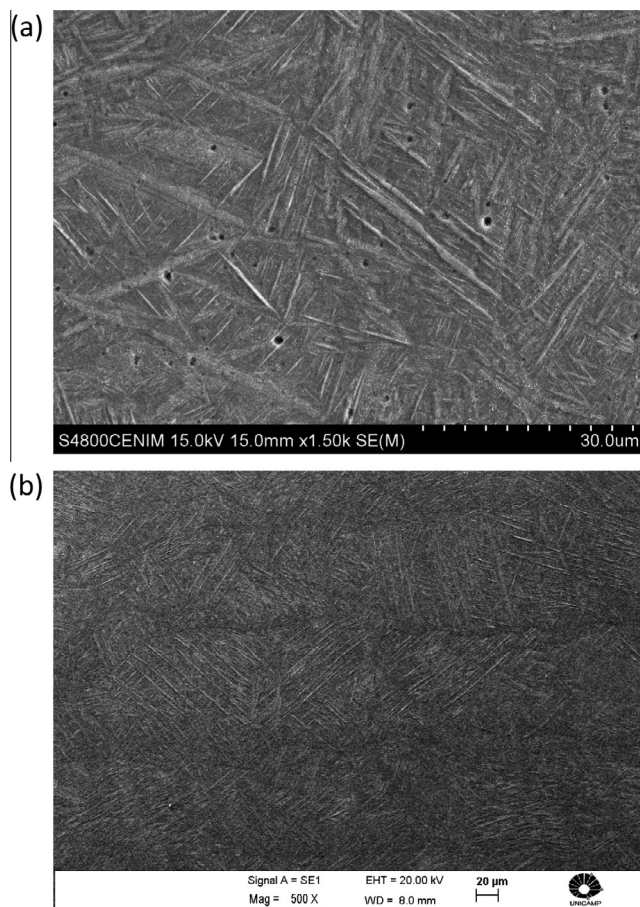


Fig. 4. Microstructure of the Ti6Al4V processed by DMLS in (a) surface and (b) cross-section.

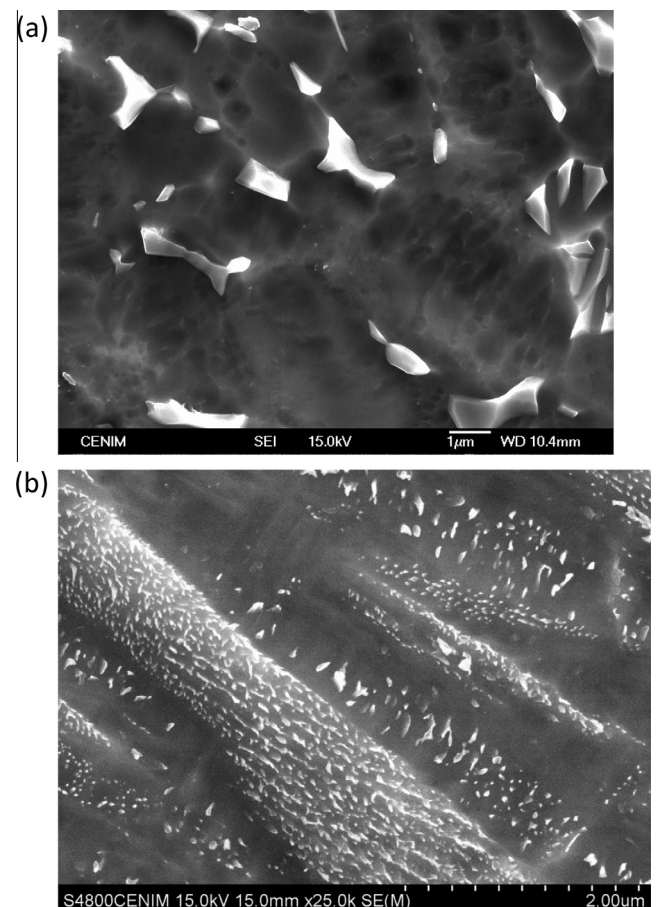


Fig. 5. (a) High magnification image of the β -phase of the solid DMLS specimen, and (b) microstructure of Ti6Al4V alloy ELI grade.

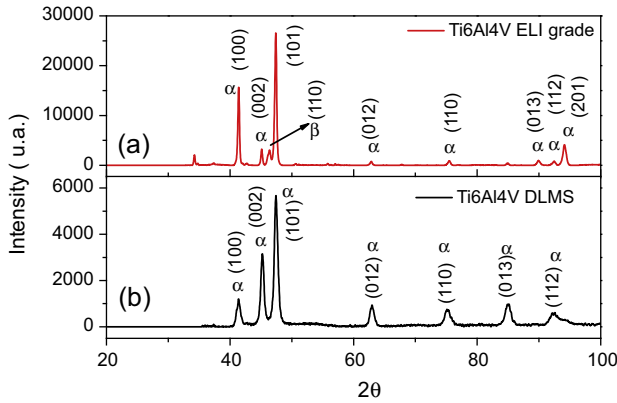


Fig. 6. X-ray diffractograms of the (a) Ti6Al4V ELI grade and (b) DMLS solid specimens.

between the elastic modulus and porosity can be estimated according to the Nielsen's relationship [44]:

$$E = E_m \frac{(1 - c)^2}{1 + \left(\frac{1}{\rho} - 1\right)c} \quad (2)$$

where E is the Young's modulus of the scaffold, E_m is the Young's modulus of solid specimen (119.53 GPa), c is the volume fraction of porosity and ρ is the geometry factor based on pore shape ($0 < \rho < 1$). For the square shape of the pores, ρ is 0.78. According to Nielsen [45] the volume concentration of pores is given by the following expression (3):

$$c = V_p / (V_s + V_p) \quad (3)$$

where V denotes volume and indexes p and s refer to the pore and solid volume respectively.

For the scaffolds the volume concentration of pores was of 41%. Using this equation, the Young's modulus for DMLS of Ti6Al4V was of 37.28 GPa, similar to the values reported by Lin et al. [42].

On the other hand, the architecture of the scaffolds allows considering these specimens as a cellular solid, and therefore estimating the porosity and Young modulus from the relative density (the density of the cellular solid divided by the density of the solid) according to the expressions defined by Gibson and Ashby [46]. In these cellular solids the fraction of pore space, its porosity, is defined by the Eq. (4):

$$\text{Porosity} = 1 - \frac{\rho^*}{\rho_s} \quad (4)$$

where ρ^* and ρ_s are the density of the cellular solid and the solid respectively.

While the Young modulus can be obtained from the expression (5):

$$\frac{E^*}{E_s} = C \left(\frac{\rho^*}{\rho_s} \right)^n \quad (5)$$

where C and n are two constants that depend on the microstructure; usually its value is 1 and 2 respectively.

According to the Eq. (4) the porosity for the Ti6Al4V DMLS specimens is about 69% and the Young modulus according to Eq. (5) is about 10.90 GPa. Even though this value is lower than that estimated from the Nielsen's equation, it still ranges within the values corresponding to the cortical bone.

The difference in Young modulus, estimated from Eqs. (2) and (5), comes from the different definition of porosity used in each case. In fact, when the porosity estimated from the relative density is used in Nielsen's equation the Young Modulus estimated is about 9.61 GPa.

Albeit, from the compressive stress–strain curves performed on the DLSM Ti6Al4V scaffolds, Fig. 7, the Young modulus obtained is about 0.341 GPa, a value closer to trabecular bone. This value obtained from the linear elasticity stage is notably lower than those previously estimated from the Nielsen and the relative density equations, respectively. Woesz et al. [47] observed that specimens having the same apparent density may have different strength, stiffness and energy absorption depending of their micro architecture. Moreover, Sercombe et al. [48] has recently pointed out that the disagreement between the properties predicted by the topological optimized model and the experimental values is consequence of the limited accuracy to reproduce the optimized cell models. This lack of accuracy is due to the local instabilities in the melt pool that can form during the laser scanning across the powder. Particularly concerning are the reduced cross sectional area and significant roughness observed on the horizontal struts that cause peak stress higher than those predicted in the optimized cell unit.

Therefore, the different results obtained from the compression tests in comparison to the values estimated using the Nielsen's and Gibson and Ashby's equations are strongly related to the architecture of the scaffold since none of these equations take into account important factors of the cell, such as the effective length of the struts, the distance between nodes and the interconnectivity (the number of struts meeting on each node). All these factors influence on load pattern distribution and the deformation stress.

In spite of these variations, the fact is that Young's modulus of these scaffolds with high open porosity of 69% of total volume fraction is almost the same as that of human cortical bone (17.3 GPa).

3.3. Surface modification and corrosion properties

Functionalization of the specimens was made by anodizing the specimens (solid and scaffolds) for five minutes at 20 V in the acid solution. As a first effect of the treatment, there is a smoothing of the surface, mainly on scaffolds. For these specimens, the average roughness decreases from $2.642 \mu\text{m} \pm 1.2 \mu\text{m}$ up to a R_a of $2.04 \pm 1.03 \mu\text{m}$.

As result of the anodization process, for both specimens, the α -phase is oxidized to form randomly arranged nanopores of 20–30 nm in diameter (Fig. 8). The EDX analysis of the porous film formed on the surface shows the presence of fluorine, between 5.7 and 6.5 at.%, and oxygen among the main components of the films.

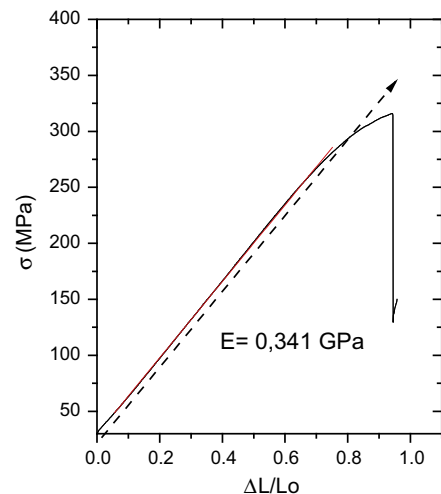


Fig. 7. Compressive stress–strain curve performed on the DLSM Ti6Al4V scaffolds.

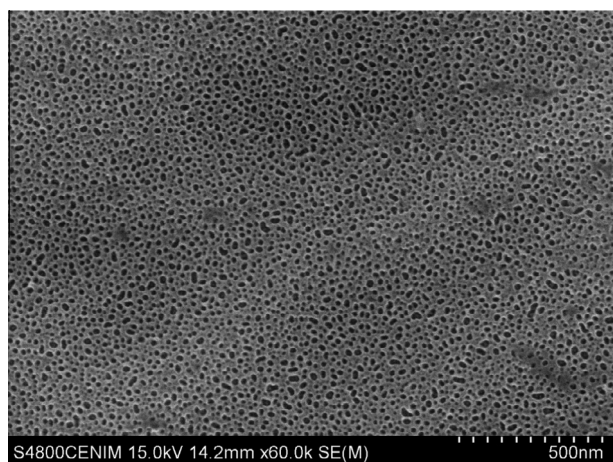


Fig. 8. Randomly arranged nanopores of 20–30 nm in diameter formed on the surface after the electrochemical oxidation.

The incorporation of fluoride in the film presents a particular interest to functionalize the surface with antibacterial properties [49].

An important difference regarding to the conventionally prepared β and $\alpha + \beta$ titanium alloys are that the small size of the β -phase obtained by DMLS technique allows fully covering the surface with a homogeneous F-TiO₂ nanoporous anodic film. As it has been previously [32] reported, anodization of Ti6Al4V ELI grade alloys do not show a nanoporous film on β -phase or it appeared recessed compared with the surrounding α matrix, revealing an irregular surface topography at the nanoscale. This situation also occurs in other $\alpha + \beta$ titanium alloys, resulting in heterogeneous TiO₂ anodic films. Kaczmarek et al [50] pointed out that this is due to a selective dissolution of the less stable phase and/or different reaction rates of the different phases of the alloys.

Cross-sectional FEG-SEM images of the titanium oxide nanoporous film are shown in Fig. 9, made by fracturing the specimen and peeling the film from the substrate. TiO₂ nanopores are well developed and aligned, with an approximately average thickness of around 100 nm. It has to be noted the relatively high thickness of the barrier layer (around 30 nm) which gives the character of nanoporous to the film unlike other anodizing processes/conditions wherein the nanotube formation occurs [15].

The electrochemical stability of the non-anodized solid Ti6Al4V DMLS specimens and the anodic films fabricated on the solid specimens was studied by potentiodynamic polarization curves

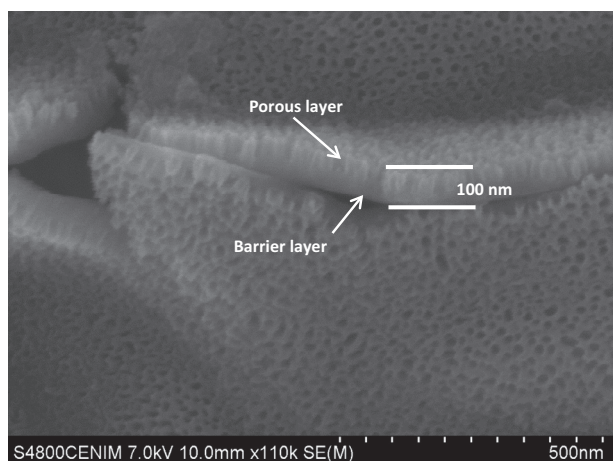


Fig. 9. Cross-sectional FEG-SEM images of the titanium oxide nanoporous film.

performed in PBS, Fig. 10. The polarization curves of the medical grade alloy are also included for comparison purposes. As can be seen, the shape of the curves for medical grade alloy and the DMLS specimen becomes almost identical. The corrosion potential, E_{corr} , of the non-anodized solid DMLS specimen is -0.420 V vs. Ag/AgCl and about -0.285 mV vs. Ag/AgCl for the medical grade Ti6Al4V.

The polarization curves also reveals a passive behavior for both type of specimens characterized by a vertical anodic branch with a passive current density $-i_{pass}$ of $7.5 \cdot 10^{-7}$ A/cm². The i_{pass} value is in the same order of magnitude than that recorded for the medical grade Ti6Al4V alloy. In the case of the functionalized surfaces, the E_{corr} of the anodic oxide layer grown on the solid DMLS specimens is about 0.140 V vs. Ag/AgCl and -0.043 V vs. Ag/AgCl for the porous film fabricated on the medical grade alloy. As in previous case, the material showed a clear passive behavior with current density one order magnitude lower than the non-anodized samples.

The non-anodized solid DMLS specimens – and to a lesser extent in the medical grade alloy – showed an increase of the current around to 1.23 V vs. Ag/AgCl (~ 1.5 V vs. ENH). There are several explanations in literature about this increase in the current, similar to the transpassivity process. According to Azevedo-Peña et al [51] these explanations could be related to the different processes that can take place on the sample surface, such oxygen evolution, rupture and formation of the film or formation of different oxides in the TiO₂ matrix. In this case, it is not due to a rupture of the passivation layer but to a change in the electronic structure of the titanium oxide; i.e. an oxidation process inside the oxide film [52,53]. Additionally, for both non-anodized specimens, the pitting potential could be as high as 2.5 V vs. Ag/AgCl, being in agreement with other results described in the literature.

So, these alloys when operating in the body fluid, have low possibilities to undergo a breakdown of passivity, since the relevant potential region in the human body is <1 V. Therefore, stable pitting corrosion is not a relevant failure mode for the materials here studied [54].

The shape of the polarization curves for the anodized specimens (DMLS solid and medical grade alloy) is very similar, revealing a clear passive region in the anodic branch, Fig. 10. The curve indicates a coarsening of the oxide layer present on the surface, with corrosion current density values about 10^{-10} A/cm² for the anodized DMLS solid sample. The anodic films fabricated on the medical grade Ti6Al4V alloy exhibited a similar passive current density ($2.1 \cdot 10^{-9}$ A/cm²). In any case, both anodic films shows higher

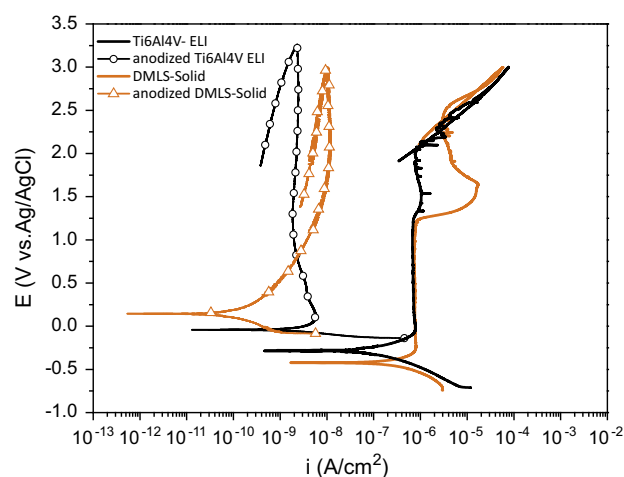


Fig. 10. Polarization curves for DMLS solid Ti6Al4V specimens and medical grade Ti6Al4V alloy before and after anodizing.

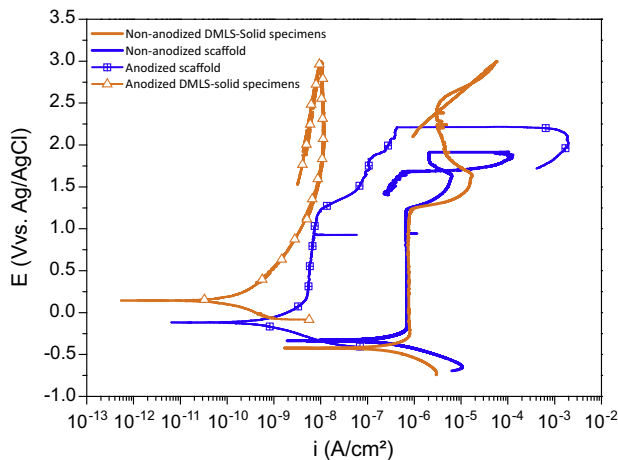


Fig. 11. Polarization curves for the solid sample and scaffolds in both conditions (non-anodized and anodized) after normalizing the current density by the real area.

stability with lower dissolution rates compared to non-anodized substrates. Therefore, this anodic film implies a great corrosion resistance with a lower amount of metallic ions delivered to the solution. This point is of great relevance for scaffolds which have a much higher specific surface area and therefore a potentially greater source of ion metal release.

It remains the question if the three-dimensional architecture of the scaffolds behaves similarly than the solid samples. Although the base material is the same alloy, the specific surface area for scaffolds is significantly higher than that for the solid specimens. Moreover, the scaffolds do not show a uniform surface as solid samples. After chemical polishing, the pore wall presents an irregular surface with a relative high roughness due to the larger amounts of attached powder particles removed. On the other hand, the geometry of the scaffolds appears to have an important influence on the corrosion resistance too, likely due to the existence of numerous edges and vertices in the sample which might have a different response in comparison to flat surfaces. So, the electrochemical measurements have to be necessarily different due to the particular architecture of the scaffold.

The area of the scaffold has been calculated from the values of the length and thickness of each strut in the rectangular prism unit cell. According to this calculation, the area of the scaffold exposed to the electrolyte is $\sim 7.7 \text{ cm}^2$.

In Fig. 11, is pictured the polarization curves for the DMLS solid samples and scaffolds in both conditions (non-anodized and anodized) after normalizing the current density by the real area. As it can be seen, the values of the passive current density are the same for both materials in the as-cast condition and very similar for the anodized samples. It is also worthy of note, the appearance of a decrease in the pitting potential for both the non-anodized and modified samples in relation with the solid samples. The pitting potential for solid samples was of 2.5 V, while for scaffolds was of 1.8 V. Thus, the scaffolds show a higher susceptibility to localized attack as result of their architecture.

Something similar happens for the anodized specimens. The solid sample do not exhibit a pitting potential even at high voltages ($>3 \text{ V}$) while anodized scaffolds present a clear pitting potential around 2.2 V. Nevertheless, as it was mentioned in previous sections the relevant potential region in the human body is clearly $<1 \text{ V}$ (42) so the higher susceptibility to localized attack of the scaffolds appears to be not so critical. Even this decrease in the pitting potential, the corrosion kinetics of both anodized DMLS samples in relation with anodized Ti6Al4V ELI grade is in the same order,

ensuring that the release of metallic ions due to corrosion is minimized in anodized DMLS samples, reducing the negative impact in its biocompatibility. As it was pointed out by Schenk [55], breakdown potentials of $>1000 \text{ mV}$ vs saturated calomel electrode are not a decisive criterion for selecting or rejecting a particular material for using as biomaterial. Additionally, it appears that the DMLS specimens modified by anodizing might exhibit bioactivity due to its morphological features. The nanoporous presence would allow for bone in growth and improved osseointegration as well as to supply antibacterial properties as result of their F content. In this sense, Lozano et al. reported that F doped nanoporous TiO_2 films grown on Ti6Al4V alloy increased proliferation as well as osteogenic gene expression and the mineralization capacity of these osteoblastic cells [56]. Therefore, it appears that the anodic film fabricated on the DMLS specimens might improve not only corrosion properties but also antibacterial and osteogenic properties useful for bone fixation of prosthetic devices.

4. Conclusion

The use of DMLS process for the production of Ti6Al4V alloy samples, allows design cellular materials with a specific geometry. The microstructure of the alloy processed by laser showed a martensitic microstructure, mainly fine needles like acicular α/α' phase with a very fine phase dispersed throughout the matrix, presumably β -phase.

The scaffolds presented a reduction in Young's modulus at values near to the bone although there are some discrepancies between compression tests and the theoretical approach, probably due to the effect of the scaffold architecture.

Surface modification by anodizing resulted in the growth of a nanoporous oxide films with a thickness of 100 nm. In comparison with the medical grade Ti alloy used as reference, the anodic film is more homogeneous, probably due to the effect of nanosize of phase on the treatment.

In addition to the mechanical advantages, both solid and scaffold samples presented a high corrosion resistance in the PBS solution. The electrochemical oxidation improves the corrosion behavior, increasing the passive current density in two orders of magnitude compared to the non-anodized material. Therefore, the anodic films showed lower dissolution rates compared to non-anodized specimens, implying reductions in the release of ions to the blood stream.

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