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L-PBF processing and characterization of a $\text{Ti}_{35}\text{Nb}_{30}\text{Zr}_{29}\text{Mo}_3\text{Ta}_3$ multiprincipal element alloy for medical implants

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ABSTRACT

This letter reports on the processing, mechanical properties, electrochemical performance and toxicity behavior of a multiprincipal element $\text{Ti}_{35}\text{Nb}_{30}\text{Zr}_{29}\text{Mo}_3\text{Ta}_3$ alloy. The recovered centimeter-sized cubes or parallelepipeds were polished before analysis. It was found that the homogeneity and yield stress of the alloys get increased when higher volumetric energy densities (VEDs) are applied during processing. The synthesized alloys also exhibited a Young modulus closer to those of bones than those usually reported on the conventional orthopedic metals (60-80 GPa for this alloy against 110 and 4-30 GPa for the Ti-6Al-4V and bone, respectively). The electrochemical corrosion assays performed at 25°C and 37°C, in sodium chloride (NaCl, 0.1 M), deoxygenated high glucose Dulbecco's Modified Eagle Medium (DMEM) and deoxygenated DMEM implemented with Fetal Bovine Serum (FBS) showed corrosion potentials (E_{corr}) ranged in the order $\text{NaCl}_{(25^\circ\text{C})} \approx \text{DMEM} + \text{PBS}_{(37^\circ\text{C})} > \text{DMEM}_{(37^\circ\text{C})}$, and impedances much larger in the DMEM and DMEM + PBS media than in NaCl. Finally, pre-osteoblasts cells cultured in the medium conditioned by the alloy did not evidence cytotoxicity effect, because no effects on the cell proliferation and morphology were observed. These data suggest the biocompatibility of this alloy, indicating no acute toxicity, which is a prerequisite for the integration of an alloy as a bioimplant.

Faced with the aging population in our modern societies and the increased risk of bone diseases and accidents in these populations, the development of long-lasting implant materials is a significant

35 public health issue. It is, nowadays, essential to adapt advanced structural materials to extend the net
36 duration of the revision surgery beyond the current limit of ten years.¹ According to the recent United
37 Nations reports, the over 60s population of the world is growing, and the proportion of the old persons
38 is expected to increase by 45% by 2050, with a life expectancy that could gain another five additional
39 years in the developed countries,² making this period of ten years before the surgical revision
40 extremely short. The problem of the longer-lasting implants also concerns people with acute and
41 chronic bone diseases while maintaining an acceptable perspective and quality of life.

42 Multiprincipal element alloys (MPEAs) are a new class of materials that offer a range of unique
43 properties, such as high strength and corrosion resistance.^{3,4} These properties make them ideal
44 candidates for designing medical devices. Moreover, by adjusting the composition of the MPEAs, it is
45 possible to create materials that are optimized for specific applications. For instance, their Young's
46 modulus can be reduced to values close to those of bones (20 to 30 GPa), without losing their yield
47 strength, thereby reducing the probability of the occurrence of osteoporosis near the implant.
48 Consequently, the MPEAs are increasingly being used in the medical industry for various
49 applications.⁵

50 In parallel, the emergence of the additive manufacturing (AM) has revolutionized the production of
51 complex and intricate structures, previously impossible to be manufactured⁶; opening thus real
52 opportunities for medical implant processing, meaning that AM allows the production of medical
53 implants tailored to the patient's needs, matching correctly the targeted function.

54 The technology behind the AM is based on the principles of the layer-by-layer deposition of materials.
55 This means that the implant is built up from a series of thin layers, and each layer is deposited on top
56 of the previous one. In this way, the AM eliminates the need for the expensive and time-consuming
57 tooling. It also enables the production of porous structures, which can serve as channels for drug
58 storage and then controlled delivery,⁷ as it allows surface texturing, which can be useful for tissue
59 integration and rejection risk reduction.⁸

60 Altogether, the AM designed MPEAs-based biomedical implants have the potential to revolutionize
61 healthcare.⁹ Combining these two innovative concepts, the implants composition and morphology

62 would be easily tailored to meet patients' anatomy, age, and gender, laying the ground for personalized
63 treatment.

64 In this study, a series of the MPEA with the nominal composition of $\text{Ti}_{39}\text{Nb}_{28}\text{Zr}_{28}\text{Mo}_{2.5}\text{Ta}_{2.5}$ (at. %) were elaborated by the laser powder bed fusion (L-PBF), using the selected laser melting (SLM) technology (see Table 1S for the actual achieved composition). By adjusting the fabrication parameters, especially the volumetric energy density (VED) during the SLM processing, the Young's modulus of the alloy was significantly reduced, without losing its yield strength, reducing thereby the probability of osteoporosis occurrence near the implant.

70 Through the processing optimization, several types of microstructural defects were identified (experimental details in the supplementary data). These were mainly unmelted powders, cracks, and pits.

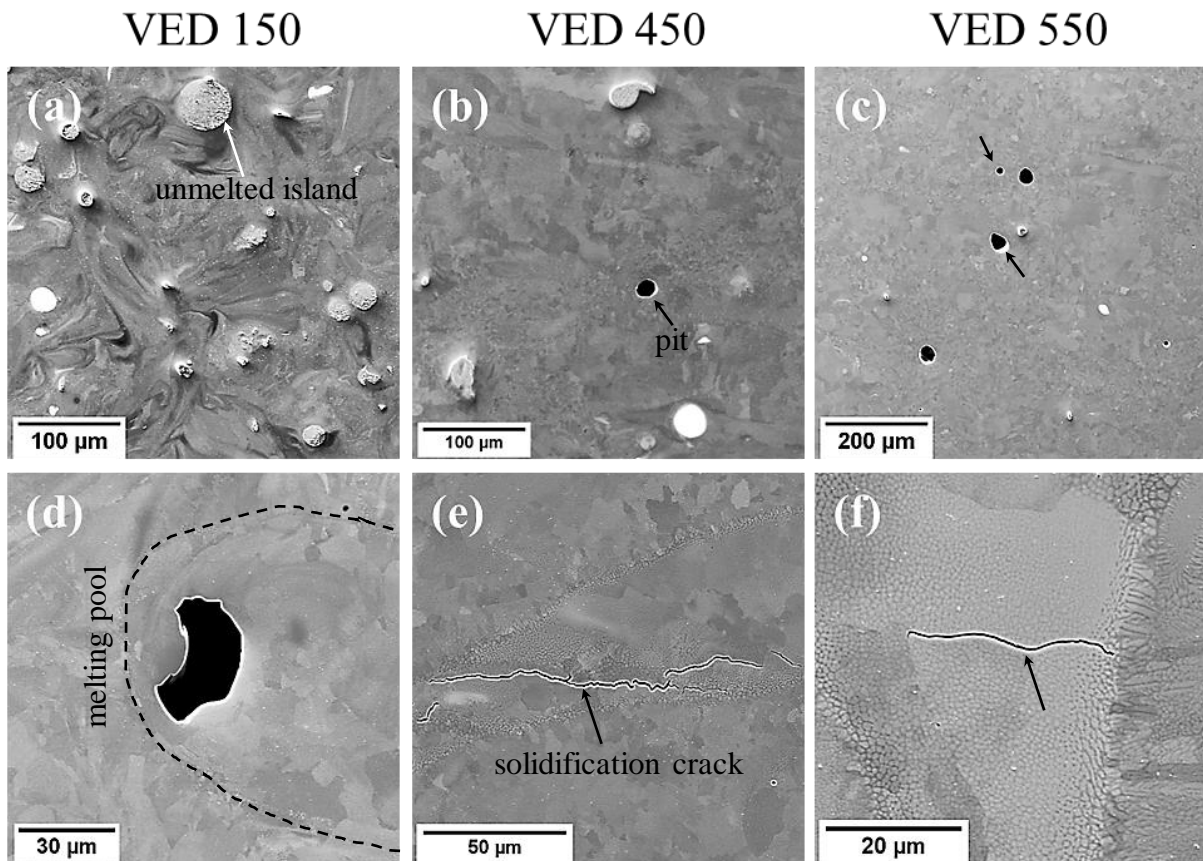
73 Melting elements like Ta, Mo and Nb with high melting points (3020, 2623 and 2477°C, respectively) is obviously arduous. The low VED resulted in the accumulation of unmelted Nb/Mo/Ta-rich islands. Scanning electron microscopy (SEM) images clearly evidence these entities by their after polishing relief and light grey contrast (as well as the Ta/Ta-rich islands by their bright light contrast), as shown in Figs. 1(a) and 1S.

78 Increasing the VED induced the Nb/Mo/Ta-rich islands solubilization, improving the homogeneity of the final alloy (Fig. 1(b, c)). Nevertheless, the solubilization of Nb/Mo/Ta into the matrix triggers the vaporization of Ti, since the melting point of Ta is close to the boiling point of Ti (3287°C). As a consequence, typical processing defects, such as keyhole porosities form. The higher the VED, the higher the keyhole porosities fraction was in the structure of the alloy. Their appearance frequency, means the coalescence of the cavities while porosities facilitate the degradation of the mechanical properties of the alloy.¹² Contrariwise, cracks cause less dramatic effects on the mechanical properties of the material. Cracking occurs either as a result of the residual stress relaxations (induced by the high cooling rate of the SLM) or the complex solidification mechanisms (involving the solidification range and liquid viscosity) (Fig. 1(e, f)). The second case usually forms short/thin intergranular cracks, primarily along the high-angle grain boundaries (HAGBs).

89 The VED affects also the grain morphology, size and size distribution. The inverse pole figure (IPF)
90 electron backscatter diffraction (EBSD) images recorded on the specimens, elaborated at the VED =
91 150, 450, and 550 J.mm⁻³, clearly evidence it (Fig. 2(a-c)). These images show heterogeneous grain
92 shapes. The degree of heterogeneity decreases with the applied VED. For the VED = 550 J.mm⁻³, a
93 relatively bimodal character was observed, while for the VED = 450 J.mm⁻³, a slight <100> texture
94 was noted.

95 On a finer scale, the grains appeared as made up of dendritic cells whose sizes increased with
96 increasing the VED, from 429 up to 516, and 740 nm, for the VED = 150, 450 and 550 J.mm⁻³,
97 respectively (Fig. 2(d-f)). The statistical details of the microstructure of the alloys can be seen in Fig.
98 2(g, h). These observations are in agreement with the existing literature data,^{10,11} where it has been
99 reported that the walls between the cells are made of accumulated geometrically necessary
100 dislocations, inducing the disorientations in the order of 2 degrees. Furthermore, the dendritic cell
101 walls were rich in Zr, while Mo was accumulated mostly inside the cells (Fig. 2S).

102



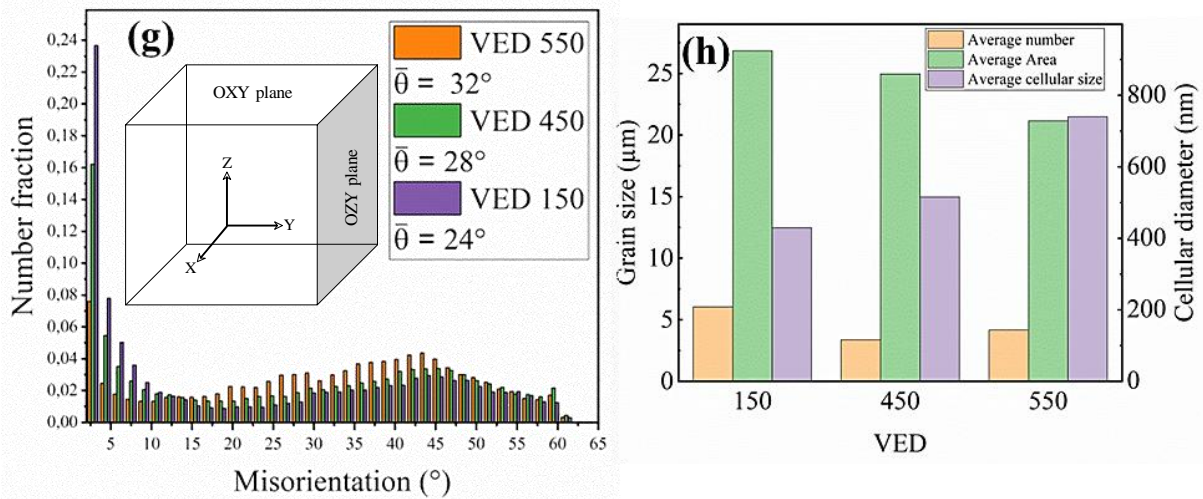
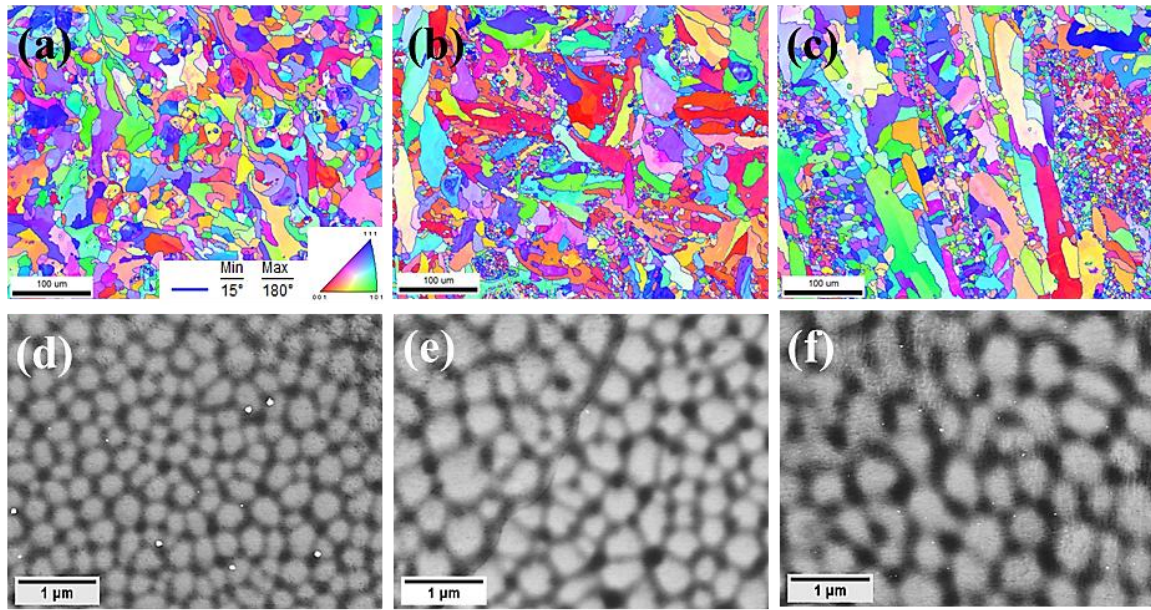
103

104 **FIG. 1.** Nature of the processing defects observed as a function of the applied VED. (a, d) 150 J.mm^{-3} ,
105 (b, e) 450 J.mm^{-3} and (c, f) 550 J.mm^{-3} .
106
107

108 The number of the HAGBs increased with increasing the VED. The average degrees of
109 misorientations were 24, 28, and 32° for the VED = 150, 450, and 550 J.mm^{-3} , respectively (Fig. 2(g)).
110 The high fraction of low angle grain boundary (LAGB) misorientation at low VED is in line with the
111 cells size given in Fig. 2(h). Indeed, smaller cell sizes (longer cell walls) increased the degree of the
112 low angle misorientation. The increase in the HAGBs' percentage coincided with the solidification
113 cracking probably due to the increase in the disorientation between the contiguous grains, in
114 agreement with the literature data.¹²

115 Apart from the evolution of the size of the dendritic cells which increased with the VED (Fig. 2(d-f)),
116 the average grain size of the alloys (measured as area fraction) decreased as the VED increased. The
117 latter is attributed to the bimodality of the alloy structure (Fig. 2(a-c)).

118



119

120 **FIG. 2.** Microstructure quantification details. (a-c) IP EBSD images superimposed to the grain
 121 boundaries map of the VED = 150, 450 and 550 $J \cdot mm^{-3}$ specimens, respectively, (d-f) SEM images of
 122 the cellular substructure of each specimen and (g, h) distribution of the misorientation across the grain
 123 boundaries, frequency of grain, and cellular size as a function of the applied VED (Z axis in Fig (g)
 124 indicates the laser beam direction).
 125

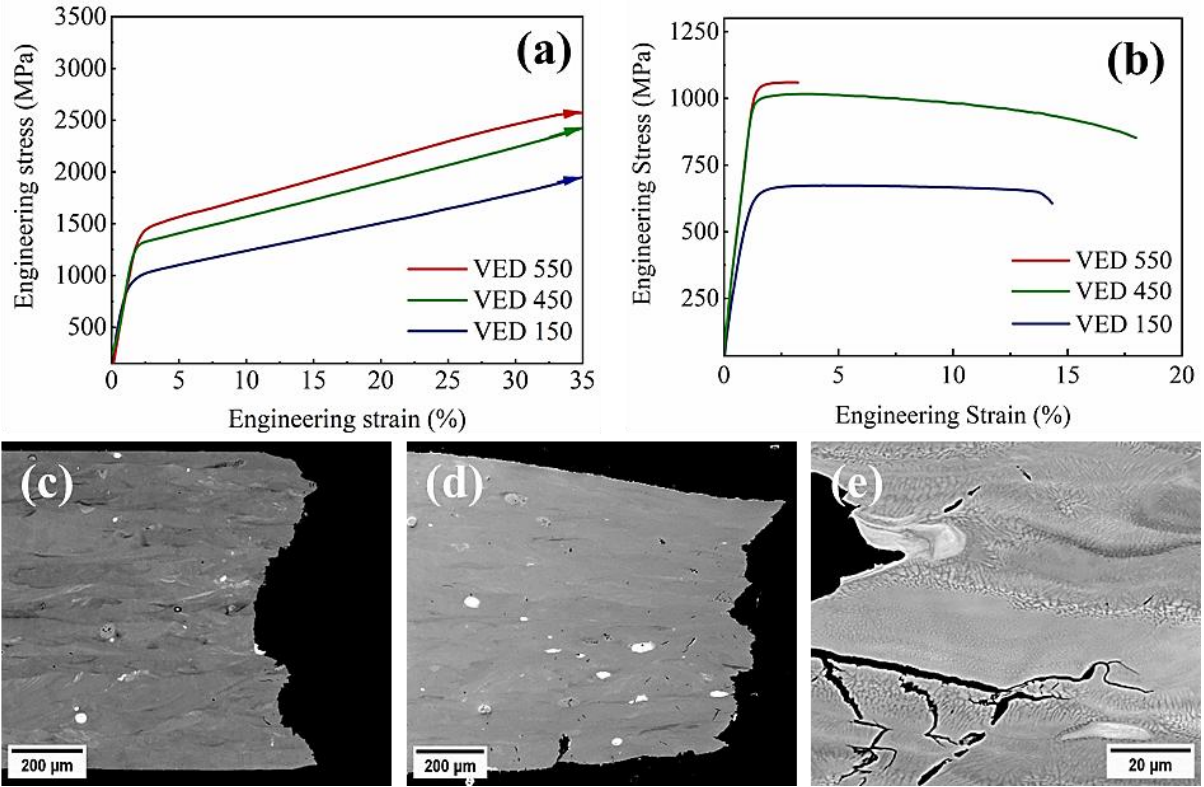
126 The results of the compression and tension tests can be compared in Fig. 3(a, b). See also experimental
 127 details in the supplementary data. Fig. 3(a) depicts that all the as-processed alloys possess a high
 128 ability to get plastically deformed. Indeed, all the specimens exhibited nominal strains well above
 129 70%. The yield stresses were found to be in the range from 900 to 1350 MPa, increasing with the VED
 130 increase. As expected, the above-mentioned processing defects did not compromise the use of these
 131 alloys in the loading conditions. Contrariwise, the tensile tests showed a high sensitivity to the
 132 microstructure. The higher the VED, the higher were the yield stress and yield strength values. For

133 instance, the $VED = 550 \text{ J.mm}^{-3}$ led to a relatively poor ductility. The related specimen is in the regime
134 with the highest keyhole porosities frequency, along with the solidification cracking. The coalescence
135 of these cavities during the straining and bridging of the microcracks into a three-dimensional
136 network, contributed to the observation of the lack of ductility. Fig. 3(c, d) illustrates the necking
137 regions of the 550 and 450 J.mm^{-3} specimens, respectively. The elongation of the Ta-rich entities into
138 a lenticular shape in the latter is evident; since opposite to the 550 J.mm^{-3} specimen, here they
139 contributed to the overall ductility of the material. Images of the generated microcracks in the 450
140 J.mm^{-3} specimen are also given in Fig. 3(d, e).

141 Here the increase in the yield strength by increasing the VED can be explained by a Hall-Petch-like
142 effect combined with a solid solution strengthening. The Hall-Petch-like effect comes from the
143 reduction of the grain size while the origin of the solid solution strengthening comes from the
144 solubilization of Nb/Mo/Ta in the matrix.

145 Table 1 summarizes the major compression and tensile loading parameters of the alloys. Here the
146 Young's modulus E values (60 to 80 GPa) are much lower than those of the materials that are
147 currently used for the orthopedic applications (CP-Ti: 105, Ti-6Al-4V: 115 and Co-Cr: 240 GPa). The
148 low E values are expected to eliminate the stress shielding effect of the material.^{13,14} Another
149 biomechanical indicator for the metallic implant materials, is the elastic strain deformation ε .¹⁵ It was
150 computed, for this study, from the tensile test data as $\varepsilon = \sigma_{YS}/E$. The obtained values were found to be
151 varying in the range from 0.87 to 1.22%, larger than those of the CP-Ti and Ti6Al4V (0.47 and 0.78%,
152 respectively), but closer to that of the as-cast TiZrNbTa (1.26%).¹⁶

153



154

155 **FIG. 3.** (a) Typical stress-strain compression test plots of the synthesized alloys along the Z axis/OXY
 156 plane (building direction), (b) tensile test plots along the OYZ plane, (c, d) failure profiles of the
 157 tensile tested 550 and 450 J.mm⁻³ specimens, respectively and (e) crack propagation along the HAGBs
 158 in the tensile tested 450 J.mm⁻³ specimen.
 159

160 **Table 1.** Some mechanical parameters of the 150, 450 and 550 J.mm⁻³ specimens.

specimen	Young modulus [GPa]	ultimate tensile stress [MPa]	yield strength [MPa]	strain to failure [%]	compression yield strength (MPa)
VED = 150 J.mm ⁻³	60	674	527	13.38	940
VED = 450 J.mm ⁻³	78	1016	950	17.99	1215
VED = 550 J.mm ⁻³	80	1061	964	3.23	1335

161

162 Altogether, these results suggest that the 150 and 550 J.mm⁻³ specimens are the best according to the *E*
 163 and ϵ criteria, respectively; for the desired application, while the 450 J.mm⁻³ one offering finally the
 164 best compromise. In the same time, the 550 J.mm⁻³ specimen exhibited the best chemical homogeneity
 165 and then very probably a better corrosion performance. The persistence of a larger number of the
 166 Nb/Mo/Ta-rich islands in the 450 J.mm⁻³ specimen compared to the 550 J.mm⁻³ one, might favor
 167 pitting corrosion, as a consequence of the (electro)chemical reactivity differences between these
 168 islands and the matrix. Also differences between the biological behaviors might be expected between

169 the islands and matrix, when contacted to bone cells. Consequently, to pursue our investigations, a
170 focus was made on the 550 J.mm^{-3} specimen.

171 The electrochemical measurements were thus performed on both 150 and 550 J.mm^{-3} specimens to
172 investigate their corrosion performance. The specimens were exposed to a 0.1 M NaCl (25°C) solution
173 and to a 37°C deoxygenated Dulbecco's Modified Eagle mammal cell culture medium (DMEM) or
174 DMEM supplemented with 20% of fetal bovine serum (FBS) (experimental details in the
175 supplementary data). After $\sim 24 \text{ h}$ of exposure, their potentiodynamic polarization curves and
176 impedance plots were recorded (Figs. 4(a, b) and 3S(a-d)). Each open circuit potential (OCP) value,
177 given in the inset of the figures is the average potential of at least three electrodes, before being
178 polarized. The corrosion potential (E_{corr}), as well as the corrosion current density (I_{corr}) values for each
179 coupon in each electrolyte are given in these figures. Along with the potentiodynamic polarization
180 curves, some selected SEM images of the pits nucleated during the polarization of the coupons in the
181 DMEM and NaCl electrolytes can be seen in Figs. 4(a) and 3S(b). (more images can be found in Fig.
182 4S).

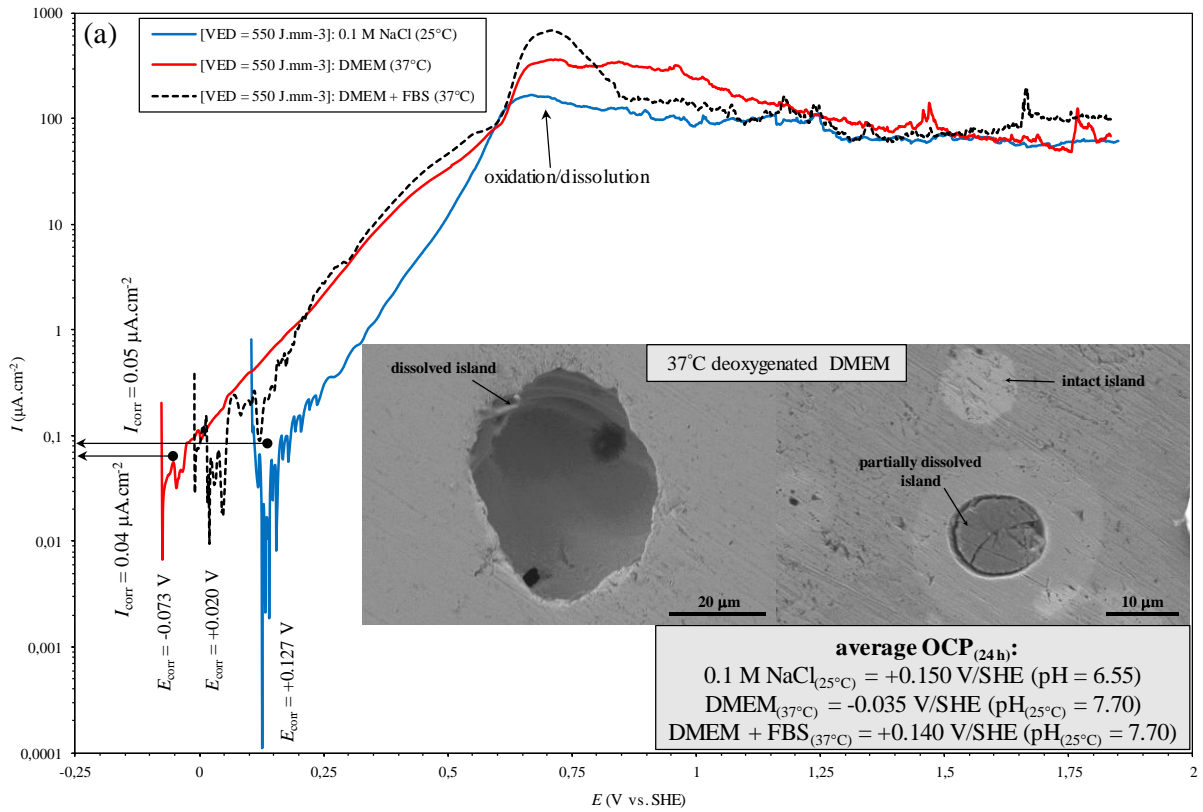
183 Interestingly, the anodic branches of all the curves (Figs. 4(a) and 3S(b)) exhibited the generation of a
184 large oxidation current, especially in $\sim +0.7 \text{ V/SHE}$. This indicates that by polarizing the coupons
185 towards more positive potentials, a considerable degree of dissolution occurs on their surfaces. The
186 OCP of the 550 J.mm^{-3} alloy in the NaCl ($\text{pH}_{(25^\circ\text{C})} = 6.55$) and DMEM + FBS ($\text{pH}_{(25^\circ\text{C})} = 7.70$) solutions
187 is the most positive ($+0.150 \text{ V/SHE}$). This potential in the DMEM ($\text{pH}_{(25^\circ\text{C})} = 7.70$) solution changes to
188 -0.035 V/SHE . The curves in Fig. 4(a) also depict that although the I_{corr} recorded in the NaCl solution
189 is slightly larger than those of the DMEM and DMEM + FBS solutions, the alloy generated a smaller
190 oxidation current in this solution, compared to the two others.

191 The recorded Nyquist plots of the 550 J.mm^{-3} coupons, show that the resistivity of the alloy in the
192 three solutions is in the order DMEM + FBS $>$ DMEM $>$ NaCl. This can be seen in the polarization
193 resistance and imaginary impedance values in Fig. 4(b). The plot recorded in the NaCl solution has an
194 incomplete/deformed semi-circle which can be fitted with an electrical circuit model based on a
195 constant phase element (CPE), parallel to a charge transfer resistance (R_{ct}) element; both in series with
196 a solution resistivity (R_s) element. In DMEM, the recorded plot consists of only a deformed semi-

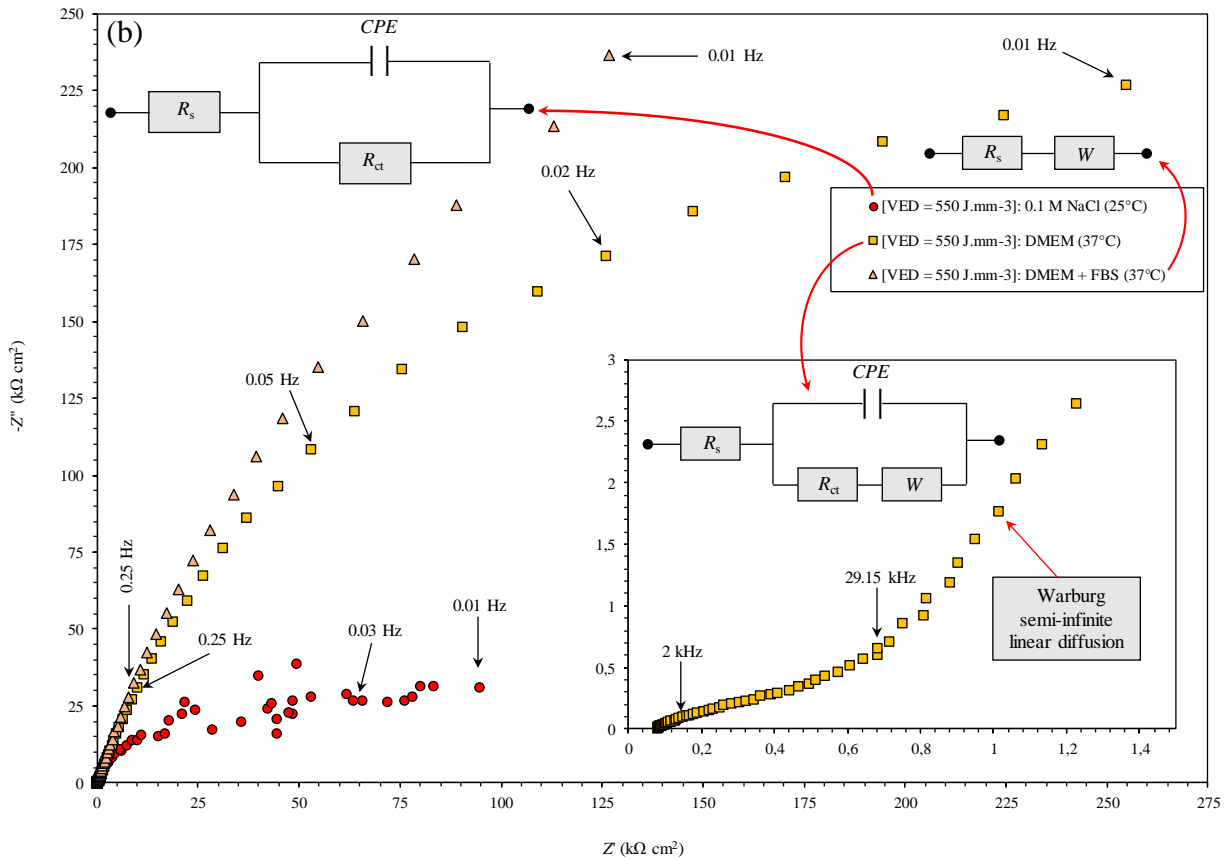
197 infinite Warburg linear diffusion impedance, that is represented with a Warburg element (W) in series
198 with a R_s (Fig. 4(b)). Here it should be noted that the slope of a classic Warburg plot is 45° and plots
199 with degrees $> 45^\circ$ indicate the existence of a greater mass transport limitation. In DMEM + FBS, the
200 recorded plot has an incomplete/deformed semi-circle in the high frequency region, followed with a
201 linear diffusion Warburg impedance, which can be modelled with an electrical circuit based on a W
202 element in series with a R_{ct} and parallel to a CPE .

203 Comparing the Bode total impedance ($|Z|$) versus frequency plots of the two alloy coupons in the
204 three electrolytes (Fig. 3S(a, d)) allows evidencing that the $|Z|$ of the 550 J.mm^{-3} coupon at the
205 minimum applied frequency is the maximum and minimum for the DMEM and NaCl solutions,
206 respectively. While, in the case of the 150 J.mm^{-3} coupon the largest and smallest minimum frequency
207 $|Z|$ belongs to the plots recorded in the DMEM and DMEM + FBS.

208 To resume the overall electrochemical results, it is clear that the 550 J.mm^{-3} alloy, has a better
209 resistivity to corrosion compared to the 150 J.mm^{-3} alloy, especially in the DMEM and DMEM + FBS
210 media, at least for the 24 h of exposure, which is useful for the desired application.



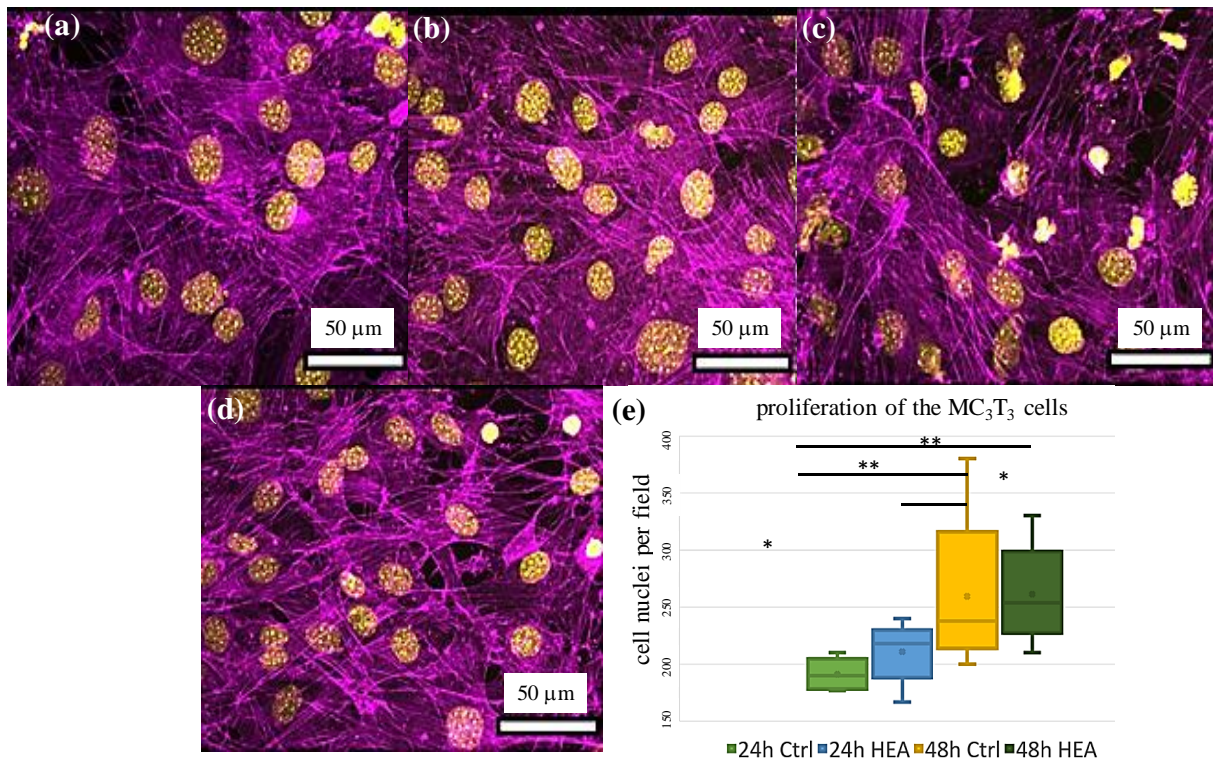
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212

213 **FIG. 4.** (a) Potentiodynamic polarization curves and (b) Nyquist plots of the 550 J.mm⁻³ alloy (in the
 214 OXY plane), recorded after 24 h exposure to a 0.1 M NaCl (25°C), a deoxygenated DMEM (37°C) and

215 a deoxygenated DMEM + FBS (80:20 (v/v)) (37°C) media. Inset: SEM images of the pits, nucleated
216 during the polarization of the alloy in DMEM.
217
218 Finally, the toxicity of the 550 J.mm⁻³ alloy was evaluated by studying the cell proliferation and
219 morphology in the alloy conditioned and normal media. The conditioned media were prepared by
220 immersing a freshly prepared 550 J.mm⁻³ coupon for 24 h in a 10 mL DMEM-F₁₂ medium.
221 Cells were thus stained (their nucleus and actin cytoskeleton in yellow and purple, respectively) (the
222 experimental details in the supplementary data) and optical images were collected and compared (Fig.
223 5). The images in Fig. 5 revealed no morphological differences between the cells cultured in the
224 control medium compared to those cultured in the medium conditioned by the alloy. This was
225 consistent with the study of the cell proliferation over 48 h. The number of the viable cells is nearly
226 identical between the cell populations, regardless of whether they were exposed to the conditioned
227 medium or not.
228 These observations are a strong indication of no acute toxicity of the alloy, suggesting its
229 biocompatibility.
230 Since it is commonly accepted that the cell proliferation performance gets enhanced by modification
231 of the surface morphology,^{17,18} the effect of the surface microstructure, in term of roughness, will be
232 further investigated. Application of the bioactive peptide coatings is also currently under investigation
233 to improve the cell viability, adhesion and proliferation.¹⁹ Up to now, only nude coupons were tested.
234 Here despite the lack of the surface optimization, the biological preliminary results supported the
235 choice of the elaborated alloy as an implant material.
236



237

238 **FIG. 5.** Optical microscopic images of the MC₃T₃ A A pre-osteoblasts cells cultured in the
 239 nonconditioned ((a) 24 h, (b) 48 h) and conditioned media ((c) 24 h, (d) 48 h) and (e) the proliferation
 240 graphic (the line within the box represents the median). ANOVA test results: n = 3, * p < 0.05, ** p <
 241 0.01.

242

243 In summary, the L-PBF processed Ti₃₅Nb₃₀Zr₂₉Mo₃Ta₃ alloys were investigated, optimizing the
 244 elaboration parameters, mainly VED, to tentatively reach a valuable microstructure, mechanical
 245 properties, electrochemical corrosion parameters and a biological compatibility toward mammal
 246 osteoblast cell proliferation, for a successful integration as bone bioimplants.

247

248 Increasing the VED induced the Nb/Mo/Ta solubilization, improving the chemical homogeneity of the
 249 processed alloys. Besides, the alloys had a high ability to get plastically deformed. They also exhibited
 250 nominal strains of >> 70%, Young modulus values much lower than those of the conventional implant
 251 alloys, elastic strains close to those of bones and yield stresses from 900 to 1350 MPa, that increased
 252 with increasing the VED, proving the capability of the alloy to be used as a bioimplant material.

252

253 Focusing on the specimens processed at high VED, their OCPs in the NaCl and DMEM + FBS media
 254 were found to be more positive, compared to DMEM, while the impedance parameters of the alloy
 were much more desirable in contact with the DMEM and DMEM + FBS. Finally, the same

255 specimen, did not induce acute toxicity and did not inhibit cell proliferation, proving its
256 biocompatibility, supporting their valuability as an implant material.

257

258 **Supplementary Material**

259 The supplementary data includes the detailed information about the elaboration process,
260 microstructure/mechanical characterization, electrochemical corrosion performance and cytotoxicity
261 behavior of the synthesized alloys.

262

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267

268 **Author Contributions**

269 Equal: conceptualization, Equal: data curation, formal analysis, writing original draft and project
270 administration.

271

272 **Data Availability**

273 The data that support the findings of this study are available within the letter and its supplementary
274 material.

275

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