Nanostructured β-phase Ti–31.0Fe–9.0Sn and sub-μm structured Ti–39.3Nb–13.3Zr–10.7Ta alloys for biomedical applications: Microstructure benefits on the mechanical and corrosion performances

Anna Hynowska a,⁎, Eva Pellicer a,⁎, Jordina Fornell a, Sergio González a, Nele van Steenberge b, Santiago Suriñacha a, Annett Gebert c, Mariana Calinc, Jürgen Eckert c, d, Maria Dolors Baró a, Jordi Sort e,⁎

a Departament de Física, Facultat de Ciències, Universitat Autònoma de Barcelona, E-08193 Bellaterra, Spain
b OCAS N.V., Pres. J.F. Kennedylaan 3, BE-9060 Zelzate, Belgium
c TU Dresden, Institute of Materials Science, D-01062 Dresden, Germany
d TU Dresden, Institute of Complex Materials, PO Box 270116, D-01171 Dresden, Germany
e Institució Catalana de Recerca i Estudis Avançats (ICREA) and Departament de Física, Universitat Autònoma de Barcelona, E-08193 Bellaterra, Spain

⁎ Corresponding authors at: Departament de Física, Facultat de Ciències, Universitat Autònoma de Barcelona, E-08193 Bellaterra, Spain.
+E-mail addresses: anna.hynowska@campus.uab.cat (A. Hynowska), eva.pellicer.icn@uab.cat (E. Pellicer), jordi.sort@uab.cat (J. Sort).

ARTICLE INFO

Article history:
Received 14 February 2012
Received in revised form 31 May 2012
Accepted 8 July 2012
Available online 14 July 2012

Keywords:
Ti-based alloys
Microstructure
Mechanical properties
Corrosion behavior

ABSTRACT

Nanostructured Ti–31.0Fe–9.0Sn and sub-micrometer structured Ti–39.3Nb–13.3Zr–10.7Ta (wt.%)-type alloys, exhibiting different microstructures and dissimilar mechanical properties, have been prepared by copper mold casting. The microstructure, mechanical behavior and corrosion resistance, in simulated body fluid, of both alloys have been investigated and compared to those of commercial Ti–6Al–4V. Nanoindentation experiments reveal that the Ti–31.0Fe–9.0Sn rods exhibit very large hardness (H ≈ 9 GPa) and high Young’s modulus. Conversely, the Ti–39.3Nb–13.3Zr–10.7Ta alloy is mechanically softer but is interesting for biomedical application because of its rather low Young’s modulus (E ≈ 71 GPa). Concerning the corrosion performance, Ti–35Nb–7Zr–5Ta shows a corrosion behavior comparable to Ti–Al6–V4, with no potential breakdown up to 0.4 V vs. Ag|AgCl. On the contrary, the Ti–31.0Fe–9.0Sn alloy exhibits a more anodic corrosion potential, but the value is still less negative than for pure elemental Fe and Ti. From all these properties and because of the absence of toxic elements in the compositions, the Ti–39.3Nb–13.3Zr–10.7Ta and Ti–31.0Fe–9.0Sn alloys are attractive for use as metallic biomaterials.

© 2012 Elsevier B.V. All rights reserved.

1. Introduction

Research in the field of biomaterials (e.g., metallic alloys, polymers, ceramics or composites), suitable for permanent or biodegradable implants, has become a highly active field during the last decades, encouraged by the increase in the quality and longevity of life that the use of these materials can provide [1]. Traditionally, 316L austenitic stainless steel and Co–Cr alloys have been employed as metallic orthopedic implants. However, these materials suffer from the drawback that they exhibit an exceedingly large Young’s modulus, E, and can be cytotoxic [2,3]. For this reason, new types of alloys, usually based on Ti, have been developed during recent years. These novel alloys exhibit a combination of excellent properties, such as low density (around 4–5 g cm−3), relatively low E ranging from 50 to 110 GPa [4], high corrosion resistance [5] and good biocompatibility [3].

From a mechanical viewpoint, the strength of Ti-based alloys is close to that of 316L steel, whereas its density is 55% lower, thus resulting in a specific strength (strength normalized to density) much higher than that of conventional metallic implants [3]. Mechanical compatibility between the implant and the surrounding tissue is also of great importance. Namely, pronounced stress transfer between the implant and bone can cause resorption and subsequent implant loosening. This biomechanical mismatch, known as “stress-shielding effect” can result in the death of the bone cells and occurs when the stiffness (or the Young’s modulus) of the implant is much higher than that of the bone (Ebone ranges between 3 and 20 GPa) [6,7]. For this reason, Ti-based alloys with rather low E values are of keen interest for biomedical applications. Indeed, the Young’s modulus of stainless steel and Co–Cr is 210 GPa and 240 GPa, respectively, thus more than twice the value of Ti-based alloys [3]. Additionally, suitable materials for implants are expected to be non-toxic and should not cause any inflammatory or allergic reaction in the human body [8]. In this sense, Ti is highly biocompatible, due in part to the formation of a thin passive oxide layer (2–3 nm) at the surface of the alloy, which protects the implant against reaction with bodily fluids.
Amongst Ti-based alloys, Ti–6Al–4V has become a widely used material in many technological applications, including the aerospace and automotive sectors, because it offers a combination of high strength, light weight, good formability and high corrosion resistance. Because of these outstanding properties as well as its cost-effectiveness, this alloy has also found applications in medical devices and as biomaterial for orthopedic implants [3]. Nevertheless, Ti–6Al–4V contains toxic elements (Al, V), which are released into the human body after long-term implantation and can eventually cause serious health problems, such as peripheral neuropathy, osteomalacia or Alzheimer’s disease [9–11].

Titanium can exist in two allotrop forms. At low temperatures atoms are disposed forming a hexagonal closed packed (hcp) crystal lattice, which is commonly referred to as α-phase, while above 883 °C atoms are arranged in a body centered cubic (bcc) crystal structure, known as β-phase. The α-to-β transformation temperature, Ta (~), in Ti alloys can either increase or decrease depending on the alloying elements. Elements such as Al or O tend to stabilize the α-phase by increasing Ta (~) and are the so-called α-stabilizers. Conversely, other elements stabilize the β-phase (e.g., V, Nb, Fe). Some elements, like Sn or Zr, behave as neutral solutes and have little effect on the transformation temperature, acting instead as strengtheners [3]. The Ti–6Al–4V alloy consists of a large fraction of hcp α-phase mixed with a small volume fraction of bcc β-phase [12]. In general, addition of β-stabilizing alloying elements causes a lowering of the Young’s modulus, an improvement of the alloy formability and an enhancement of the corrosion resistance [9]. This makes β-Ti alloys better for biomedical applications than α-Ti alloys. It has been shown that Nb, Zr, Ta, Sn or Fe is suitable alloying elements that can be introduced in the alloy composition to reduce the Young’s modulus of bcc Ti without decreasing the strength [13]. These elements are non-toxic and can thus be used for implant applications [14]. Amongst the β-type Ti alloys, the Ti–Nb–Zr and Ti–Nb–Zr–Ta families stand out from the rest because of their rather low E value [12,15]. In particular, the Ti–35Nb–7Zr–5Ta (wt.%) alloy (also known as “TiOsteum”) exhibits a Young’s modulus of 55 GPa, the lowest reported to date for Ti-based biocompatible materials [16]. However, usually the hardness, H, of β-type alloys is not particularly high and attempts have been made to increase it, for instance by adding elements with strengthening potential (e.g., Fe) [17], tuning the oxygen content [16], or engineering suitable microstructures with high strength [18,19].

The strength of metallic alloys depends not only on the crystallographic phases composing the microstructure but also on the size of the crystals and the presence of structural defects [20]. Nanocrystalline metals exhibit larger hardness and quite often better corrosion and wear resistance than coarse-grained ones [21]. Combination of large hardness with low Young’s modulus (i.e., high H/E ratio) is indicative of good wear resistance [22]. This is an important parameter since orthopedic implants are expected to suffer from abrasion with bone and hard tissues and the formation of wear debris can result in inflammatory reactions [23]. However, nanocrystalline alloys sometimes exhibit limited plasticity at room temperature. To increase it, micrometer-sized particles composed of a softer phase are sometimes embedded in the nanostructured harder matrix, forming a bimodal microstructure [18,19,24,25]. In this sense, the formation of β-Ti/αFe composites consisting of β-Ti micrometer-sized dendrites embedded in a nanoeutectic matrix has been reported to result in optimum mechanical properties [26]. Addition of Sn to this system has been shown to further enhance its strength [27,28].

In this work, we investigate the mechanical properties and corrosion resistance, in simulated body fluid, of two nanostructured phase alloys with dissimilar microstructure and mechanical properties (i.e., Ti–31.0Fe–9.0Sn and Ti–44.3Nb–8.7Zr–12.3Ta), and compare them with commercial Ti–6Al–4V. These compositions were selected for several reasons. First, the Ti–Nb–Zr–Ta system is known to exhibit rather low Young’s modulus (i.e., good biomechanical compatibility with bone) but moderate hardness, whereas the Ti–Fe–Sn system shows high yield strength but also exceedingly high Young’s modulus, which could eventually lead to stress shielding effects. A material combining low Young’s modulus with high strength would be ideally suited for biomedical implants. With this aim, we produced an alloy from the Ti–Nb–Zr–Ta system with larger Nb and Ta percentages than those in “TiOsteum” (the alloy composition of the Ti–Nb–Zr–Ta system showing the lowest Young’s modulus), since both Nb and Ta should favor an increase of hardness and plasticity. In fact, although the properties of TiOsteum has been extensively investigated, those of other Ti–Nb–Zr–Ta alloys have been largely overlooked. On the other hand, Ti–31.0Fe–9.0Sn has been also investigated in some detail because of its interesting ultra-fine grained microstructure [27,28]. However, the mechanical properties of this alloy have been mainly investigated only by means of macroscopic compression experiments but not with nanoindentation. Here, we make use of the same nanoindentation experimental setup and the same experimental load-unload conditions to investigate both alloy families, with the aim of allowing for a better comparison of the mechanical behavior between the different materials. In particular, nanoindentation experiments reveal that the Ti–31.0Fe–9.0Sn cast rods exhibit very large hardness (H ≥ 8 GPa) and relatively high Young’s modulus. Conversely, the Ti–39.3Nb–13.3Zr–10.7Ta alloy is interesting because of its rather low Young’s modulus (E ≈ 71 GPa), thus favoring its biomechanical compatibility with bone, while exhibiting reasonable hardness, higher than that of the “TiOsteum” alloy. Remarkably, both alloys show larger H/E ratios (i.e., better wear resistance) than commercial Ti–6Al–4V. Concerning the corrosion behavior, neither Ti–39.3Nb–13.3Zr–10.7Ta nor Ti–31.0Fe–9.0Sn presents passivity breakdown. The Ti–39.3Nb–13.3Zr–10.7Ta system shows comparable corrosion potential to Ti–6Al–4V, whereas the Ti–31.0Fe–9.0Sn alloy exhibits more anodic corrosion potential values. From all these properties and because of the absence of toxic elements in their compositions, the Ti–39.3Nb–13.3Zr–10.7Ta and Ti–31.0Fe–9.0Sn alloys are appealing for their use as metallic biomaterials.

2. Materials and methods

Cylindrical rods of 2 and 3 mm in diameter with compositions Ti–39.3Nb–13.3Zr–10.7Ta and Ti–31.0Fe–9.0Sn (wt.%), respectively, were prepared by Cu-mold suction casting. The master alloys were obtained from a mixture of high-purity elements (>99.99 wt.%) by arc-melting in a Ti-gettered high purity Ar atmosphere on a water-cooled Cu hearth. The samples were structurally characterized by X-ray diffraction (XRD), using a Philips XPert diffractometer with monochromatic Cu Kα radiation. The patterns were analyzed by means of a full-pattern fitting procedure (Rietveld method) with the Microstructural Analysis Using Diffraction (MAUD) computer software [29,30]. An EVO-Zeiss scanning electron microscope (SEM), equipped with an energy dispersive X-ray spectrometer (EDX, Link ISIS-200) was used for microstructure observation and compositional analyses. Transmission electron microscopy (TEM) imaging was also performed, using a Jeol-JEM 2011 system operated at 200 kV.

Nanoindentation experiments were carried out on the as-cast samples using a UMIS equipment from Fischer-Cripps laboratories, with a Berkovich pyramidal-shaped indenter tip applying a maximum load of 250 mN. A load holding period of 20 s was added before unloading and the thermal drift was always kept below ± 0.05 nm s⁻¹. At least 50 indentations on each sample were performed to verify the accuracy of the indentation data. Prior to the nanoindentation tests the specimens were carefully polished to mirror-like appearance using diamond paste. The method of Oliver and Pharr was used to determine the hardness and the reduced Young’s modulus [31,32]. Proper corrections for the contact area (calibrated with a fused quartz specimen), the instrument compliance, and the initial penetration depth were applied. The
hardness was obtained from the ratio between the maximum load, \( P_{\text{Max}} \), and the contact area of the indent, \( A \), i.e.:

\[
H = \frac{P_{\text{Max}}}{A}.
\]  

From the initial unloading slope, the contact stiffness, \( S \), was determined as follows:

\[
S = \frac{dP}{dn}
\]

where \( P \) and \( n \) denote the applied load and the penetration depth during nanoindentation, respectively. The elastic modulus was then evaluated based on its relationship with the contact area, \( A \), and the contact stiffness:

\[
S = \beta \frac{2}{\sqrt{\pi}} E I \sqrt{A}
\]

Here, \( \beta \) is a constant that depends on the geometry of the indenter (\( (\beta = 1.034 \) for a Berkovich indenter) [33]) and \( E_{\text{i}} \) is the so-called reduced Young’s modulus, defined as:

\[
E_{\text{i}} = \frac{1 - \nu^2}{E_{\text{e}}} + \frac{1 - \nu^2}{E_{\text{p}}} - \frac{1}{E_{\text{l}}}
\]

The reduced modulus takes into account the elastic displacements that occur in both the specimen, with Young’s modulus \( E \) and Poisson’s ratio \( \nu \), and the diamond indenter, with elastic constants \( E_{\text{e}} = 1140 \) GPa and \( \nu_{\text{e}} = 0.07 \). Finally, the elastic/plastic indentation energies were also calculated. The total mechanical work done by the indenter during loading, \( U_{\text{tot}} \), was calculated from the area enclosed between the loading indentation segment and the displacement axis. This energy is defined as the sum of the elastic, \( U_{\text{el}} \), and plastic, \( U_{\text{pl}} \), energies:

\[
U_{\text{tot}} = U_{\text{el}} + U_{\text{pl}}
\]

The values of \( U_{\text{el}} \) were obtained from the area enclosed between the unloading segments and the plastic deformation axis [34]. The elastic recovery was evaluated as the ratio between the elastic and the total (plastic + elastic) energies during nanoindentation, \( U_{\text{el}}/U_{\text{tot}} \).

The corrosion behavior of the as-cast samples was investigated by electrochemical polarization measurements using a PGSTAT120 Autolab potentiostat/galvanostat (Ecochemie). Prior to the measurements, slices from the Ti–31.0Fe–9.0Sn and Ti–39.3Nb–13.3Zr–10.7Ta alloy were cut and carefully ground with emery paper (SiC) down to grit 4000 and further polished with 6 μm diamond suspension. Subsequently, the samples were degreased in acetone and finally cleaned with distilled water. Electrochemical corrosion experiments were performed in naturally aerated simulated physiological Hank’s balanced salt solution (HBSS) at 37.5 °C. The composition of the HBSS solution was 8.0 g dm⁻³ NaCl + 0.4 g dm⁻³ KCl + 0.04788 g dm⁻³ Na₂HPO₄ + 0.06666 g dm⁻³ KH₂PO₄ + 0.185 g dm⁻³ CaCl₂ · 2H₂O + 0.09767 g dm⁻³ MgSO₄ + 0.35 g dm⁻³ NaHCO₃ + 1.0 g dm⁻³ D-glucose. A typical three-electrode cell configuration was used. The reference electrode consisted of a double junction Ag/AgCl electrode filled with 3 M KCl inner solution and 1 M NaCl interchangeable outer solution (E(SHE) = +0.210 V). A platinum foil acted as the counter electrode. Before each polarization scan, the sample was immersed in the electrolyte and left for at least 2 h for stabilization until variations of the potential became smaller than 0.01 V h⁻¹. The stabilized value was considered to be the open-circuit potential (OCP). Afterwards, the potential was swept toward the anodic direction starting from 300 mV below to the OCP at a scan rate of 0.1 mV s⁻¹. The corrosion current density \( (i_{\text{corr}}) \) values were determined using the Tafel extrapolation method [35]. The polarization resistance, \( R_p \), was used to determine the resistance of the alloys against corrosion [36]. The values of \( R_p \) were determined as:

\[
R_p = \left( \frac{\Delta E}{\Delta t} \right)_{\text{d}E/dt = 0}
\]

where \( \Delta E \) is the variation of the applied potential around the corrosion potential and \( \Delta t \) is the resulting polarization current. If the Tafel slopes (anodic slope, \( a \), and cathodic slope, \( b \)) are known, the corrosion current, \( i_{\text{corr}} \), can be calculated using the Stern–Geary equation [35,36]:

\[
i_{\text{corr}} = \frac{2.303 \times b \times c}{b + c} \left( \frac{1}{R_p} \right)
\]

The mechanical properties and the corrosion behavior of the nanostructured Ti–31.0Fe–9.0Sn and Ti–39.3Nb–13.3Zr–10.7Ta alloys were compared with those of commercial Ti–6Al–4V [37].

3. Results and discussion

3.1. Microstructure

SEM images (backscattered electrons) of the Ti–39.3Nb–13.3Zr–10.7Ta and Ti–31.0Fe–9.0Sn as-cast alloys are shown in Fig. 1(a) and (b), respectively. The Ti–39.3Nb–13.3Zr–10.7Ta sample is composed of dark and light gray regions of a few micrometers in lateral size. TEM images (shown as insets) reveal the presence of several sub-μm grains within the micrometer-sized regions, together with the occurrence of different types of dislocations. EDX compositional analyses reveal that the light gray grains are rich in Nb and Ta whereas the darker ones are enriched in Zr and Ti (Table 1). The lighter contrast comes mainly from the high Ta content, since the atomic weight of this element (180.95 g mol⁻¹) is the largest amongst all the constituent elements of this alloy. In spite of this two-region microstructure, the XRD pattern only shows a few Bragg’s peaks corresponding to the β-phase (see Fig. 2). This indicates that both regions consist of β-Ti phases with different amounts of dissolved Zr, Ta and Nb. However, the cell parameters of the light and dark gray regions are very similar (a = 0.33258 nm); therefore, the resulting XRD peaks become overlapped.

The microstructure of the Ti–31.0Fe–9.0Sn alloy is quite different. In this case, a composite-like morphology is observed. Two types of micrometer-sized dendrites (with dark gray and bright contrast) are embedded in an ultra-fine eutectic matrix. EDX analyses reveal that the bright dendrites contain a high Sn content, whereas the gray ones are rich in Ti. High amounts of Fe are detected in the nanoeutectic phase (see Table 1). Analysis of the XRD pattern (Fig. 2) reveals the presence of mainly two crystallographic phases in this alloy: bcc-Ti (I3m) (i.e., β-phase) and bcc-Ref (Pm3m). The β-phase comprises both the gray dendrites and one of the phases of the eutectic matrix, while bcc-Ref is the other phase in the eutectic matrix [38]. The third phase (corresponding to the brightest dendrites) is hardly detectable by XRD but it presumably corresponds to hexagonal Ti₃Sn phase (P6₃/mmc) [39,40].

Fig. 2 also shows the XRD pattern of the commercial Ti–6Al–4V alloy, which mainly consists of an α-Ti phase with small amounts of β-Ti phase. Rietveld refinement of the XRD patterns using the MAUD software allows determining the cell parameters, crystallite sizes and microstrains of the different phases. To properly account for the differences in chemical composition (i.e., cell parameter) and crystallite size, two distinct β-Ti phases were considered in the refinement of the Ti–31.0Fe–9.0Sn XRD patterns (one for the dendrites and the other for the eutectics). Conversely, since the two β-Ti regions in the Ti–39.3Nb–13.3Zr–10.7Ta sample are virtually indistinguishable by
which indicates that the TiFe phase in the eutectic regions is probably reported for the equiatomic Ti

The cell parameter in the (175 pm) and Ta (170 pm), as compared to Ti (160 pm). An increase of

This is probably related to the larger covalent radii of Nb (164 pm), Zr (175 pm) and Ta (170 pm), as compared to Ti (160 pm). An increase of the cell parameter in the β-Ti phase will thus occur if such elements (Nb, Zr or Ta) enter this phase in substitution of Ti atoms. Conversely, the cell parameter in the Ti phase is slightly larger in the phases forming the eutectic matrix of the Ti–31.0Fe–9.0Sn alloy.

XRD, they were both adjusted as a single β-Ti phase. As shown in Table 2, the unit cell parameter for the Ti–31.0Fe–10.7Ta alloy is slightly larger than the value tabulated for pure bcc Ti (a=0.33065 nm) [41]. This is probably related to the larger covalent radii of Nb (164 pm), Zr (175 pm) and Ta (170 pm), as compared to Ti (160 pm). An increase of the cell parameter in the β-Ti phase will thus occur if such elements (Nb, Zr or Ta) enter this phase in substitution of Ti atoms. Conversely, the cell parameters of the β-phases in the Ti–31.0Fe–9.0Sn alloy are larger than the value tabulated, probably because of the small atomic radii of Fe (132 pm) and Sn (139 pm) as compared to Ti. The lattice parameter of the TiFe phase (a=0.30363 nm) is slightly larger than the value reported for the equiatomic Ti–Fe composition (a=0.2976 nm) [42], which indicates that the TiFe phase in the eutectic regions is probably enriched in Ti. Also remarkable from Table 2 is that the crystallite sizes in all existing phases fall within the sub-50 nm range. Particularly small crystallite size values are obtained in the Ti–31.0Fe–9.0Sn alloy, in agreement with its rather refined microstructure, as observed by SEM imaging (Fig. 1). The values of microstrains range between 8·10–4 and 5·10–3, being a bit larger in the phases forming the eutectic matrix of the Ti–31.0Fe–9.0Sn alloy.

3.2. Mechanical properties

Fig. 3 shows representative nanoindentation curves corresponding to the Ti–6Al–4V, Ti–39.3Nb–13.3Zr–10.7Ta and Ti–31.0Fe–9.0Sn alloys. The largest value of maximum penetration depth, obtained at the end of the loading segment, is observed for the Ti–39.3Nb–13.3Zr–10.7Ta alloy, indicating that this material possesses the lowest hardness value amongst the three investigated systems. Conversely, the Ti–31.0Fe–9.0Sn alloy is the mechanically hardest one. Furthermore, the initial slope of the unloading indentation segment, i.e., the contact stiffness, is also higher for the Ti–31.0Fe–9.0Sn alloy and lower for the Ti–39.3Nb–13.3Zr–10.7Ta sample, indicating that the former exhibits the largest reduced Young’s modulus whereas the latter possesses the lowest one (see Eq. 3).

For each sample, the hardness and the reduced Young’s modulus have been calculated from an average of 50 indentations performed using a maximum load of 250 mN. Such relatively high value of applied load created indents at the surface of the specimens which are sufficiently large to embrace all the phases/regions composing the investigated alloys (see

Table 1

<table>
<thead>
<tr>
<th>Sample</th>
<th>Phases</th>
<th>Element concentration (wt.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>β-Ti (light gray)</td>
<td>Ti Fe Sn Nb Ta</td>
<td>33.2 45.0 7.8 14.0</td>
</tr>
<tr>
<td>β-Ti (dark gray)</td>
<td>β-Ti (dendrites)</td>
<td>43.0 29.9 22.1 5.0</td>
</tr>
<tr>
<td>TiSn</td>
<td></td>
<td>59.7 16.7 23.6</td>
</tr>
<tr>
<td>Eutectic regions</td>
<td></td>
<td>48.8 50.2 1.0</td>
</tr>
</tbody>
</table>

Table 2

<table>
<thead>
<tr>
<th>Sample</th>
<th>Phases</th>
<th>a (nm)</th>
<th>c (nm)</th>
<th>&lt;D&gt; (nm)</th>
<th>(c/1/2)^2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti–6Al–4V</td>
<td>α-Phase</td>
<td>0.23144</td>
<td>0.46762</td>
<td>46</td>
<td>0.0008</td>
</tr>
<tr>
<td>Ti–39.3Nb–13.3Zr–10.7Ta</td>
<td>β-Phase (Ti, dendrites)</td>
<td>0.33258</td>
<td>–</td>
<td>38</td>
<td>0.0019</td>
</tr>
<tr>
<td>Ti–31.0Fe–9.0Sn</td>
<td>β-Phase (Ti, eutectic)</td>
<td>0.30384</td>
<td>–</td>
<td>23</td>
<td>0.0009</td>
</tr>
<tr>
<td></td>
<td>β-Phase</td>
<td>0.32612</td>
<td>–</td>
<td>15</td>
<td>0.0050</td>
</tr>
<tr>
<td></td>
<td>β-Phase</td>
<td>0.30033</td>
<td>–</td>
<td>20</td>
<td>0.0031</td>
</tr>
</tbody>
</table>
The indentation curves (Fig. 3) and the load-displacement responses (Fig. 4) show that the Ti-31.0Fe-9.0Sn alloy exhibits the lowest Young's modulus (105 GPa), as compared to Ti-39.3Nb-13.3Zr-10.7Ta (116 GPa) and Ti-31.0Fe-9.0Sn (126 GPa), which are characterized by similar mechanical properties. The difference in mechanical behavior between these alloys can be attributed to the microstructure, particularly in the phases composing the eutectic regions. It is worth mentioning that the hardness of Ti-39.3Nb-13.3Zr-10.7Ta alloy is larger than that in Ti-31.0Fe-9.0Sn, since this alloy is also composed of a large fraction of the β-type phase. Instead, the large Er in this particular alloy is probably mainly related to the presence of Fe.

The Ti-39.3Nb-13.3Zr-10.7Ta alloy also exhibits the lowest Young's modulus (E<sub>ν</sub> = 71 GPa) among the three investigated alloys (see Table 3). The commercial Ti-6Al-4V material possesses a Young's modulus in excess of 120 GPa, much larger than the value for Ti-39.3Nb-13.3Zr-10.7Ta (E<sub>ν</sub> = 71 GPa), probably because of the large percentage of α-phase contained in this alloy. The presence of β-stabilizing elements (such as Nb) in Ti-39.3Nb-13.3Zr-10.7Ta favors the reduction of Young's modulus [8,12,15]. However, following this reasoning, a similarly low value of E<sub>ν</sub> would be expected for Ti-31.0Fe-9.0Sn, since this alloy is also composed of a large fraction of the β-phase. Instead, the large E<sub>ν</sub> in this particular alloy is probably mainly related to the presence of Fe. The Young's modulus of Fe (E<sub<f</sub> = 211 GPa) is much larger than that of Ti (E<sub<f</sub> = 116 GPa) [41]. Conversely, Nb and Zr exhibit rather low Young's moduli (E<sub<f</sub> = 105 GPa and E<sub<f</sub> = 68 GPa). Hence, not only the microstructure (grain size, morphology) but also the elastic properties of the constituent elements determine the overall Young's modulus of the investigated alloys.

Table 3 also lists the values of H/E<sub>ν</sub>, H/Er, and H/E<sub>f</sub> for the different alloys. As expected, due to its large hardness, the Ti-31.0Fe-9.0Sn alloy exhibits the highest H/E<sub>ν</sub> and H/Er ratios. Furthermore, in spite of its relatively low hardness, the Ti-39.3Nb-13.3Zr-10.7Ta alloy also shows a H/E<sub>ν</sub> ratio larger than the commercial Ti-6Al-4V alloy. This ratio, related to the elastic strain to failure, has been shown to be a suitable parameter to describe the wear resistance of a given material [22]. Similarly, the ratio H/E<sub>f</sub> (sometimes referred to as the yield pressure [21,47]) is also indicative of the wear resistance and is as well larger for the Ti-39.3Nb-13.3Zr-10.7Ta alloy than for Ti-6Al-4V. Our results are in good agreement with friction wear tests at different loads performed in various families of Ti-based alloys immersed in a Ringer's solution, which revealed that the weight loss of
Table 3
Summary of the values of hardness (H), reduced Young’s modulus (E_r), H/E_r, U_el/U_tot and U_pl/U_tot (where U_pl, U_el and U_tot denote the plastic, elastic and total indentation energies, respectively), corresponding to the Ti–6Al–4V, Ti–39.3Nb–13.3Zr–10.7Ta and Ti–31.0Fe–9.0Sn alloys extracted from the nanoindentation curves.

<table>
<thead>
<tr>
<th>Sample</th>
<th>H (GPa)</th>
<th>E_r (GPa)</th>
<th>H/E_r</th>
<th>H/E_r^2 (GPa)</th>
<th>U_el/U_tot</th>
<th>U_pl/U_tot</th>
<th>U_el/U_tot</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti–6Al–4V</td>
<td>5.0±0.1</td>
<td>121±3</td>
<td>0.041±0.001</td>
<td>0.009±0.001</td>
<td>0.254±0.005</td>
<td>0.746±0.014</td>
<td></td>
</tr>
<tr>
<td>Ti–39.3Nb–13.3Zr–10.7Ta</td>
<td>4.4±0.2</td>
<td>71±2</td>
<td>0.062±0.002</td>
<td>0.017±0.003</td>
<td>0.353±0.013</td>
<td>0.647±0.023</td>
<td></td>
</tr>
<tr>
<td>Ti–31.0Fe–9.0Sn</td>
<td>8.9±0.3</td>
<td>147±4</td>
<td>0.069±0.001</td>
<td>0.033±0.004</td>
<td>0.342±0.009</td>
<td>0.658±0.018</td>
<td></td>
</tr>
</tbody>
</table>

Ti–6Al–4V was generally larger than that of Ti–Nb–Zr–Ta alloys [48], although other studies showed the opposite trend [49]. Such discrepancies may be ascribed to differences in the microstructure. Although the α-phase is intrinsically harder than the β-phase, the presence of crystallite sizes in the nm-range (as in our case) can lead to reasonable hardness values without affecting too much the Young’s modulus, thus resulting in reasonably high H/E_r ratios. In the case of Ti–31.0Fe–9.0Sn alloy, the existence of a two-phase microstructure (including the presence of eutectic regions containing a hard intermetallic phase) favors the increase of the wear resistance [50].

The elastic recovery and plasticity index, related to the nanoindentation elastic and plastic energies, are also parameters that characterize the mechanical behavior of biomaterials. The elastic recovery, (i.e., U_el/U_tot), indicates how much energy is released from a material after being loaded. In turn, U_pl/U_el often is related to the intrinsic plasticity of a given alloy [51]. As shown in Table 3, although a large hardness value is observed for Ti–31.0Fe–9.0Sn, the highest elastic recovery is obtained for the Ti–39.3Nb–13.3Zr–10.7Ta alloy. The elastic recovery of Ti–6Al–4V is the smallest amongst the investigated alloys, in spite of its intermediate hardness which lies between that of Ti–39.3Nb–13.3Zr–10.7Ta and Ti–31.0Fe–9.0Sn. Actually, it has been shown that a general correlation between H and U_pl/U_el does not necessarily hold [52,53], a trend which is also observed in the present case (Table 3).

Concerning the U_pl/U_tot ratio, the values of the β-type alloys are larger than those reported for Ti–Cu–Zr–Pd bulk metallic glasses [53]. The Ti–6Al–4V alloy shows the highest U_pl/U_tot ratio indicating larger intrinsic plasticity, probably because of the presence of ductile Al. However, typical implants utilized for bone replacement are not subject to pronounced plastic strains. Hence, from a mechanical viewpoint, the β-type alloys investigated here are better in many aspects than commercial Ti–6Al–4V.

3.3 Corrosion behavior

Fig. 5 shows representative potentiodynamic polarization curves of the as-cast Ti–31.0Fe–9.0Sn and Ti–39.3Nb–13.3Zr–10.7Ta samples, along with that of the commercial Ti–6Al–4V alloy, for the aim of comparison. The corresponding corrosion potential, E_corr, the corrosion current density, J_corr, and the polarization resistance, R_p, values are listed in Table 4. Both Ti–39.3Nb–13.3Zr–10.7Ta and commercial Ti–6Al–4V alloys show similar E_corr values, close to 0 V, in agreement with other works in which the corrosion behavior of Ti–35Nb–7Zr–5Ta in Ringer’s solution was assessed [54], but with different active-to-passive transitions. The J_corr value for Ti–39.3Nb–13.3Zr–10.7Ta is slightly higher than that of Ti–6Al–4V due to the higher slope. Interestingly, the R_p of the former is a little bit higher and no clear breakdown is observed in the anodic branch up to 0.4 V, unlike commercial Ti–6Al–4V, which shows an active-to-passive transition at ~0.12 V originating from structural or chemical changes in the passive layer that increases its permeability and ultimately leads to higher current density levels. Nevertheless, randomly distributed fluctuations can be seen on the potentiodynamic curve of Ti–39.3Nb–13.3Zr–10.7Ta, whose origin is not yet well understood. On the other hand, the Ti–31.0Fe–9.0Sn alloy shows more negative E_corr (~0.175 V) and higher J_corr values, though passivity breakdown does not occur either. Apart from the composition, which is different, the fact that its average crystallite size is smaller compared to the Ti–39.3Nb–13.3Zr–10.7Ta and Ti–6Al–4V alloys could inherently lead to a poorer corrosion performance due to the larger volume fraction of interfaces [55]. Nevertheless, E_corr is more positive than the values of pure iron (~0.542 V vs. Ag/AgCl) [39] and pure titanium (~0.373 V vs Ag/AgCl) [56]. This suggests that not only the composition but also the microstructure plays a key role on the corrosion performance of the material. It should be noted that the corrosion behavior of various Ti–Fe–Sn alloys has been evaluated in different electrolytes with pH in the range of 1–13, especially in chloride-containing strong acidic solutions [40], but their behavior in neutral physiological solutions has not been explored yet. The E_corr value observed for Ti–31.0Fe–9.0Sn is close to the value for Ti–Fe–Sn alloys with lower Sn content tested in 0.3 M chloride-free borate buffer electrolyte (pH 8.4) (~0.207 V vs. Ag/AgCl). At this point it should be noted that although this material has potential to be used in the biomedical field, an eventual allergenic reaction to this alloy [57] as well as the release, if any, of metal cations to the bodily fluid warrants an in-depth investigation. Preliminary in vitro assays with different cell lines indicate that this alloy is not cytotoxic.

Secondary electron (SE) and corresponding backscattered electron (BSE) images of Ti–31.0Fe–9.0Sn and Ti–39.3Nb–13.3Zr–10.7Ta samples both before and after the corrosion tests are shown in Figs. 6 and 7, respectively. Concerning the Ti–31.0Fe–9.0Sn alloy, a rather unaltered surface was observed at the end of the polarization experiment (Fig. 6(c) and (d)), featuring a composition close to the nominal one (i.e., before corrosion) (see Table 5). Only a few NaCl particles, coming from waste Hanks’ solution, were encountered on the surface (see inset of Fig. 6(c)). On the contrary, the surface of the Ti–39.3Nb–13.3Zr–10.7Ta alloy after the corrosion tests showed a larger amount of corrosion products, as evidenced topographically in the SE image and compositionally in the BSE image by the spotty darker areas [Fig. 7(c) and (d)]. The oxygen content was found to be large both locally and globally (Table 6), indicating that an oxide layer has been probably formed on the specimen’s surface. Moreover, chlorine was detected in large amounts by EDX-spot analyses in the particles spread on the alloy surface (see inset of Fig. 7(c)).

Fig. 5. Potentiodynamic polarization curves for Ti–6Al–4V, Ti–39.3Nb–13.3Zr–10.7Ta and Ti–31.0Fe–9.0Sn alloys in Hank’s solution electrolyte at a scan rate of 0.1 mV s⁻¹.
4. Conclusions

An in-depth comparative study of the microstructure, the mechanical properties and the corrosion behavior in a physiological environment of two different nanostructured \( \beta \)-type Ti-based alloys, synthesized by coppe r mol dc a s t i n g , a s well a s t h e widely used commercial Ti–6Al–4V alloy, has been carried out. While one of the newly developed alloys (Ti–31.0Fe–9.0Sn) is interesting because of its large hardness (\( H \approx 9 \text{ GPa} \)), the other material (Ti–44.3Nb–13.3Zr–12.3Ta) is appealing because of its low Young’s modulus (\( E_r = 71 \text{ GPa} \)). Both alloys exhibit better wear resistance (i.e., larger \( H/E_r \) ratios) than commercial Ti–6Al–4V. From the point of view of biocorrosion, none of the new alloys show potential breakdown within the explored potential window (up to 0.4 V), whilst the Ti–6Al–4V does. Both the corrosion potential, \( E_{corr} \), and the corrosion current density, \( j_{corr} \), values exhibited by the Ti–39.3Nb–13.3Zr–10.7Ta alloy are similar to those of commercial Ti–6Al–4V, whereas a shift in \( E_{corr} \) towards more negative values and increased \( j_{corr} \) values are observed for Ti–31.0Fe–9.0Sn, probably due to its smaller average crystallite size. In any case, the surfaces exposed to the bodily fluid do not become particularly damaged. From all these properties, the \( \beta \)-type alloys investigated here are found to be better in many aspects than commercial Ti–6Al–4V. In addition, due to the absence of toxic elements, these materials are well suited for a variety of biomedical purposes.

Acknowledgments

The authors wish to thank the Servei de Microscòpia of the Universitat Autònoma de Barcelona for the technical assistance. We also acknowledge the Catalan DGR (2009-SGR-1292), the Spanish MICINN (MAT2011-27380-C02-01), the EU (FP7PEOPLE-2010-ITN-264635, BioTiNet) and the German Science Foundation (SFB-TR79) for financial support. M.D.B. acknowledges partial financial support from an ICREA-Academia Award.

Table 4

<table>
<thead>
<tr>
<th>Composition</th>
<th>( j_{corr} ) (A cm(^{-2}))</th>
<th>( E_{corr} ) (V)</th>
<th>( R_p ) (( \Omega ))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti–6Al–4V</td>
<td>( 4.1 \times 10^{-7} )</td>
<td>(-0.019)</td>
<td>( 1.8 \times 10^{+4} )</td>
</tr>
<tr>
<td>Ti–39.3Nb–13.3Zr–10.7Ta</td>
<td>( 1.6 \times 10^{-6} )</td>
<td>(-0.021)</td>
<td>( 6.5 \times 10^{+4} )</td>
</tr>
<tr>
<td>Ti–31.0Fe–9.0Sn</td>
<td>( 8.7 \times 10^{-6} )</td>
<td>(-0.175)</td>
<td>( 1.7 \times 10^{+4} )</td>
</tr>
</tbody>
</table>

Fig. 6. SEM images corresponding to the Ti–31.0Fe–9.0Sn alloy, before corrosion [(a) SE and (b) BSE] and after corrosion [(c) SE and (d) BSE]. The inset in (c) corresponds to a particle (corrosion product) deposited at the specimen’s surface.

Fig. 7. SEM images corresponding to the Ti–39.3Nb–13.3Zr–10.7Ta alloy, before corrosion [(a) SE and (b) BSE] and after corrosion [(c) SE and (d) BSE]. The inset in (c) corresponds to a particle (corrosion product) deposited at the specimen’s surface.

Table 5

<table>
<thead>
<tr>
<th>Element concentration (wt.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti</td>
</tr>
<tr>
<td>-----</td>
</tr>
<tr>
<td>Before corrosion (overall composition, Fig 6a)</td>
</tr>
<tr>
<td>After corrosion (from a large region of the surface area—without corrosion products, Fig. 6c)</td>
</tr>
<tr>
<td>After corrosion (from a particle deposited on the sample’s surface, i.e., corrosion product, Fig. 6c inset)</td>
</tr>
</tbody>
</table>
Before corrosion
(overall composition, Fig. 7a)

<table>
<thead>
<tr>
<th>Element concentration (wt.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti</td>
</tr>
<tr>
<td>36.7</td>
</tr>
</tbody>
</table>

After corrosion
(from a large region of the surface area — Fig. 7c)

<table>
<thead>
<tr>
<th>Element concentration (wt.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti</td>
</tr>
<tr>
<td>30.7</td>
</tr>
</tbody>
</table>

After corrosion
(from a particle deposited on the sample's surface, i.e., corrosion product, Fig. 7c inset)

<table>
<thead>
<tr>
<th>Element concentration (wt.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti</td>
</tr>
<tr>
<td>10.7</td>
</tr>
</tbody>
</table>

References


Table 6
Chemical composition of the Ti–39.3Nb–13.3Zr–10.7Ta alloy surface, obtained by EDX, both before and after corrosion experiments.

<table>
<thead>
<tr>
<th>Element concentration (wt.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti</td>
</tr>
<tr>
<td>39.3</td>
</tr>
</tbody>
</table>

Before corrosion
(overall composition, Fig. 7a)

<table>
<thead>
<tr>
<th>Element concentration (wt.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti</td>
</tr>
<tr>
<td>30.7</td>
</tr>
</tbody>
</table>

After corrosion
(from a large region of the surface area — Fig. 7c)

<table>
<thead>
<tr>
<th>Element concentration (wt.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti</td>
</tr>
<tr>
<td>10.7</td>
</tr>
</tbody>
</table>

After corrosion
(from a particle deposited on the sample's surface, i.e., corrosion product, Fig. 7c inset)

<table>
<thead>
<tr>
<th>Element concentration (wt.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti</td>
</tr>
<tr>
<td>10.7</td>
</tr>
</tbody>
</table>