Elaboration of Ti-based Biocompatible Alloys Using Nb, Fe and Zr as Alloying Elements

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Increasing biocompatibility of implant materials is an important factor in developing better and long-lasting implants that function in a very close way to real tissue and bone. Various alloys have been chosen due to their biocompatibility, such as: stainless steels, titanium alloys and nickel or cobalt alloys. According to the alloying elements it is possible to change the material properties to fit into various application niches such as pacemaker devices, stents, biosensors, dental or bone implants and others. Some alloying elements confer higher biocompatibility than others and the commonly used alloys include elements that can be detrimental to human health such as Nickel, Vanadium and Cobalt. Choosing alloying elements such as Nb, Fe and Zr in order to replace the commonly used metals reduces the risks of accumulation of various substances that can damage the human tissues and lead to health complications. The proposed alloys are elaborated in a Five Celes melting furnace under argon atmosphere in order to create a more homogeneous material with lesser defects and inclusions. The cast alloys are then analyzed through modern methods such as SEM, XRD, EDS and their mechanical properties such as hardness and strength and these properties are compared to that of the bone in order to assess mechanical reliability.

Keywords: biocompatible, TiNbFeZr, β-titanium, alloys

The definition of biomaterials squares mainly on the compatibility with human tissue meaning that they can remain in contact with the body without suffering corrosion due to the fluids they are exposed to [1].

Today, approximately 70% to 80% of implant materials are of metallic origin. Biocompatible alloys such as Co-Cr and stainless steels are used as biomaterials in implant devices, but the titanium alloys display the strongest biocompatibility [2].

The reason behind titanium’s strong biocompatibility is the formation of a passivating oxide layer on the part’s surface exposed to the atmosphere that blocks the corrosion of the material or alloy and ensures that it does not slowly diffuse into the body.

The titanium alloys can be differentiated with respect to their crystal structure. Three categories can be discerned and applied in medical devices: alpha (α) - with a HCP crystal structure; alpha plus beta (α+β) - with HCP and BCC structures; and beta (β) [3]. An important factor in assessing the mechanical properties of the alloy is the cooling rate from high temperatures. The β - type titanium alloys are obtained through fast cooling while the same cooling rate would result in a martensitic structure in an α+β alloy which displays incompatible mechanical properties [4].

Although titanium exhibits the highest corrosion resistance it is necessary to alloy it in order to obtain the mechanical properties suitable for prosthetics [5].

Other advantages that come with the use of titanium as a base alloy for biomaterials are that it has a low density (approximately 4.5g/cc) [6], its alloys are resistant to pitting attack and crevice corrosion [7] and it does not reduce the healing time of wounds due to the fact that it does not exist in the body chemistry, which leads to less diffusion and a longer life of the implant.

One of the most commonly used titanium alloy is Ti-6Al-4V, which makes up 45% of the production, while pure titanium covers 30% and other alloys the remaining 25% [8, 9]. Although this is the case, it has been reported that the Al and V present in these alloys can sometimes diffuse into the body and cause long term health problems [10].

In terms of general performance, the β alloys display higher strength and a lower elastic modulus than the α + β titanium alloys, and they have become the focus of research in biocompatible materials in the last decades for implant purposes, all the while using biocompatible alloying elements such as Nb, Ta, Zr, Mo [11].

The choice of the addition of Nb, Fe and Zr as alloying elements is due to the fact that they are all β-stabilizing elements for titanium and Zr has the added bonus of also lowering the modulus of elasticity [12].

Experimental part

High purity metal precursors were used for the elaboration of the alloys (Ti> 99.9%; Nb> 99.9%; Fe > 99.6% and Zr> 99.9%) in order to reduce the influence of impurities over the specimens microstructure. In order to obtain a homogeneous distribution of the elements throughout the specimens, they were elaborated in a Fives Celes ALU 600 (France) furnace in vacuum, controlled argon atmosphere and cold crucible which also allows the removal of oxidation of the materials. The chosen working parameters were a nominal power of 25 kW under a vacuum of 5x10⁻⁵ bar and argon atmosphere at 1 bar.

A total of 4 specimens have been elaborated with different concentrations of the alloying elements (Nb, Fe, Zr) in the titanium matrix, that are given in table 1. The composition was also checked through Energy Dispersive Spectroscopy.

The purpose of the higher Fe content in the alloy was to reduce the Nb requirement and maintain a lower cost for the final product, while the Zr was added in order to lower the modulus of elasticity.

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After elaboration, the specimens were cooled in the crucible and then processed for analysis. As for the sample preparation, they were cut, mounted and polished using a complete line of specialized equipment from Struers (Denmark). The surfaces were smoothed up to mirror-like appearance and then metallographically etched using an etching solution for aluminum with a base of HF. The chemical etching was performed in order to better observe the surface structure and grains of the specimens.

The samples were also analyzed through Scanning Electron Microscopy coupled with Energy Dispersive Spectrometry (SEM – EDS, FEI Quanta 450 FEG, USA) and also through X-ray Diffraction (XRD, Panalytical X’Pert PRO MPD, Netherlands) in order to determine the crystal structure and composition of the alloys. SEM analysis was performed under high vacuum, with a voltage of 30 KV, while XRD was performed using high intensity Cu-Kα radiation (\(\lambda = 1.54065 \text{ Å}\)).

The biocompatibility testing was performed in a solution of 0.1M lactic acid with 0.1M NaCl following the standard procedure given by ISO 10271:2011. The testing was conducted for 168 h by immersion in the solution at 37°C.

The melting of the raw materials was a fast process with good homogenization of the melt due to the furnace specifications and design. After the chemical etching the samples were analyzed by SEM and EDS. The results are shown in figure 1 for all four specimens.

The EDS analysis shows, through mapping of the elements present in the alloys, that in the case of Alloy #1, #2 and #3 the Fe tends to agglomerate at the grain boundary together with the Zr, while Nb is fully dispersed into the material structure. This is also visible through the SEM micrographs where it is possible to discern the existence of compounds placed at the grain boundaries.

In the case of Alloy #4, one may see that all elements are dispersed homogeneously into the structure. One can also see that the structure is displayed in a dendritical pattern.

### Table 1

<table>
<thead>
<tr>
<th>Specimen / Composition</th>
<th>Ti (wt%)</th>
<th>Nb (wt%)</th>
<th>Fe (wt%)</th>
<th>Zr (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alloy #1</td>
<td>61.35</td>
<td>22.62</td>
<td>12.86</td>
<td>3.17</td>
</tr>
<tr>
<td>Alloy #2</td>
<td>63.6</td>
<td>21.08</td>
<td>11.69</td>
<td>3.62</td>
</tr>
<tr>
<td>Alloy #3</td>
<td>61.38</td>
<td>22.54</td>
<td>11.68</td>
<td>4.4</td>
</tr>
<tr>
<td>Alloy #4</td>
<td>65.3</td>
<td>20.3</td>
<td>11.21</td>
<td>1.81</td>
</tr>
</tbody>
</table>

The polarization curves were acquired from -100mV/sce up to +1.5mV/sce with a potential scanning rate of 1mV/s.

### Results and discussions

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Fig. 1b. SEM-EDS analysis of alloy #2

Fig. 1c. SEM-EDS analysis of alloy #3
which is specific to β-phase titanium. The elaboration conditions of high temperature and relative fast cooling support the formation of β-phase Ti along with the alloying elements which are all beta-stabilizers.

In the case of the first 3 alloys, the Zr content was higher with each new composition which lead to more segregation of the iron into the grain boundary area. In the case of the fourth alloy it is observable that the lower Zr concentration lead to the removal of the secondary compound in the material.

The specimens were subsequently analyzed through XRD at a step size of 1° and a scan rate of 0.02°/s with a scan range of 10 to 100°. The results of this analysis are shown in figure 2.

One may see on the XRD results that each sample displays the main Ti and TiNb peak followed by several smaller intensity peaks that correspond to the compounds that form in the matrix. In the case of the first 3 alloys, as seen in the EDS analysis, Zr and Fe show a strong affinity for each other and lead to the formation of the FeZr compound which segregates at the edge of the grain boundaries. In the case of Alloy #4, which has only a 1.8wt.% concentration of Zr, it can be seen that the FeZr is completely assimilated by the Ti matrix and leads to the formation of the Fe(TiZr). The XRD strongly supports the findings of the SEM imagery.

Due to the fact that Alloy #4 shown the most homogeneous structure, it was submitted to hardness testing with a result of 361 HV, which is very close to that of commercially available Ti-6Al-4V (approximately 340 HV) [13].

Alloy #4 was also subjected to a corrosion test in order to assess the biocompatibility of the material. The specimen was submersed in an artificial saliva solution for 168 h in order to observe if it exhibits any corrosion features. On visual analysis the sample kept its metallic shine that resulted from the earlier polish. The solution was analyzed using X-Ray Fluorescence (S8 Tiger, Bruker, USA) and it did not contain any of the elements present in the alloy.

When comparing the results of the corrosion test to these of a Ti-Nb-Fe alloy [14] it is found that Alloy #4 shows a higher corrosion rate per year than the alloy without Zr in its composition (corrosion rate of 2.54 µm/y).

Figure 3 shows the potentiostatic EIS curves of Alloy #4 in the first hour and after 168 h in the testing solution. One may see that the Zmod value drops which means that the
Fig. 3. Potentiostatic EIS results for Alloy #4 after 1 hour in artificial saliva and 168 h, respectively.

Table 2

<table>
<thead>
<tr>
<th>$E_{corr}$ ($mV/sce$)</th>
<th>$i_{corr}$ ($\mu Acm^{-2}$)</th>
<th>Anodic slope (V/decade)</th>
<th>Cathodic slope (V/decade)</th>
<th>Corrosion rate $10^{-5}$ inch/year</th>
</tr>
</thead>
<tbody>
<tr>
<td>84</td>
<td>89.7</td>
<td>793.6$e^{-3}$</td>
<td>206.8$e^{-3}$</td>
<td>60.1</td>
</tr>
</tbody>
</table>

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References

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