New TiZrNbTaFe high entropy alloy used for medical applications

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Abstract. The paper considers a new concept of alloy with high entropy (HEA) for biomedical applications. HEAs are different from the conventional metallic materials by more than five alloying elements, in proportions between 5% and 35% at., which may form simple solid solutions with BCC and/or FCC phases instead of complicated intermetallic ones. These specific features provide HEA with excellent mechanical properties (hardness, strength, malleability), oxidation and corrosion resistance, with potential applications in diverse industrial areas. The present tendency in the newest titanium alloys generation is the decrease of elasticity modulus, with the maintaining of high mechanical characteristics. Thus, the paper considers the system TiZrNbTaFe for biomedical applications obtained by powder metallurgy (PM) route, because HEAs prepared by this method show a greater homogeneity in their microstructure compared to the segregated microstructure of melted and cast HEAs. The influence of milling time, compaction and sintering on the microstructure and mechanical and corrosion properties of the new TiZrNbTaFe alloy were investigated. The obtained properties have shown a better mechanical biocompatibility in order to use this high entropy alloy as orthopedic or dental implants. The mechanical properties of the obtained alloys are better than those of biomaterials that are used in present.

1. Introduction
Beta titanium alloys (β-type Ti-based alloys) are the most flexible class of titanium alloys used for manufacturing orthopaedic and dental devices, as they offer the highest strength to weight ratios, lower modulus and very attractive combinations of strength, toughness and fatigue resistance, compared to α-type and α+β-type Ti-alloys [1-8]. These characteristics made them adequate to be applied in medicine. The science of tissue-implant interactions, tissue engineering, as well as recent advances in biology and medicine, identified a new concept of titanium alloys as bio-functional materials, these alloys being the most suitable biomaterials for replacing failed hard tissue up to now. Material candidates for biomedical applications must fulfil requirements such as high corrosion resistance in physiological media, biocompatibility, osseointegration and favourable mechanical properties (e.g. Young modulus similar to that of the human bone, high fatigue strength).
Mechanical biocompatibility of biomaterials is regarded as an important factor, and therefore the development of β-titanium alloys, which are advantageous when considering this criterion, is still underway. The β stability can also be maintained with the aid of alloying elements such as niobium (Nb), tantalum (Ta), zirconium (Zr), molybdenum (Mo), vanadium (V), iron (Fe) etc [9]. Thus, in the last years Nb, Ta and Zr are considered the most favourable non-toxic and non-allergenic alloying elements for β-titanium alloys for biomedical applications. From the β-type Ti-based alloy systems the most reported biomaterials are: Ti-Nb-Ta-Mo, Ti-Nb-Ta-Sn, Ti-Nb-Ta-Zr, Ti-Nb-Sn, Ti-Zr-Cr-Mo, Ti-Mo-Nb, Ti-Mo-Ta, Ti-Ta, Ti-Zr-Mo and Ti-Nb-Zr-Ta, [10-18]. Many of these alloys contain various percentages of Nb, Ta, Zr, Mo, Sn or Cr. These alloys are generally obtained by melting and casting followed by heat treatment or sintering followed by hot-forging and cold rolling. They have an elastic modulus between 42-93 GPa, tensile strengths between 597 – 1037 MPa, yield strengths 547 - 908 MPa and elongations of 13-19% [19,20].

Recently, a new Ti-based alloy (Ti-Nb-Zr-Ta-Fe) was reported, with a 2425 MPa yield strength and a Young modulus of 52 GPa. The materials were obtained after heat treatment at 960°C, with dual β structure and grain size average of 200-300 nm [21]. A promising alternative for obtaining Ti-based alloys, which is intensively investigated in the recent years, is powder metallurgy. This approach uses elemental or pre-alloyed powders and leads to the manufacturing of porous titanium parts at a much lower processing temperature, with a more precise control of the process variables and pore size, as well as of the physical and chemical characteristics. The most investigated Ti-based alloys obtained by this method are: Ti-Nb, Ti-Nb-Zr, Ti-Nb-Ta-Zr, Ti-Mo, Ti-Nb-Mo, Ti-Nb-Ta-Sn, Ti-Nb-Ta-Mn, Ti-Nb-Zr-Ta-Si etc [22-31]. The microstructures of these alloys reveal the stable β-phase, as well as nanocrystalline intermetallic compounds embedded in the amorphous matrix with nano-crystallites, and superior mechanical properties: low elastic modulus 50-80 GPa, ultimate tensile strengths of 665 – 705 MPa, yield strengths of 580-630 MPa, compressive strengths of 50-130 MPa, hardness between 290 and 660 HV and a porosity around 30%.

In the present work a TiZrNbTaFe multicomponent high-entropy alloy developed via powder metallurgy was investigated. The alloy exhibited remarkable corrosion resistance in simulated body fluids and it proves to be a promising alternative for biomedical applications.

2. Experimental methodology and used materials
High purity elemental powders of Ti, Nb, Zr, Ta and Fe, with a grain size of 45 μm and nominal composition of Ti40-Nb20-Ta20-Ta10-Fe10, were used to obtain the alloy. The elemental powders were mechanically alloyed in a planetary ball mill for 20 and 40 hours, at 200 rpm, in stainless steel vials using balls with 15 mm in diameter, at a ball-to-powder ratio of 10:1. The powders were charged into the vials in argon atmosphere using a MBraun MB200 glove-box in order to prevent their oxidation. The elemental powders, as well as the ball-milled materials, were analysed by X-ray diffraction (XRD) and by electron microscopy (SEM and EDAX). After milling, the alloyed powders were consolidated in a hydraulic press at 200 MPa and sintered at 1000°C for 2-3 hours.

The Vickers microhardness of the cast TiZrNbTaFe alloy samples was measured at room temperature using a PMS 73 testing machine. In order to determine the average hardness of the alloy, several indentations (100 g load) were performed on the surface of the samples.

The corrosion behavior of the cast alloys was carried out in in simulated body fluids (Ringer lactate solution) through the potentiodynamic polarization method, using an AUTOLAB potentiostat – galvanostat equipped with a specialized corrosion testing software which includes the PGSTAT302N, BA and SCAN250 modules.

3. Results and discussions
Three nominal compositions were investigated for obtaining Ti-Zr-Nb-Ta-Fe alloys. The chemical compositions of the resulting HEAs are presented in table 1.
Table 1. Chemical composition of the multicomponent alloy and their densities.

| Elemental powder | BIOHEA 1 | BIOHEA 2 | BIOHEA 3 |
|------------------|----------|----------|----------|
|                  | at.%     | wt%      | at.%     | wt%      | at.%     | wt%      |
| Ti               | 40       | 24.04    | 40       | 24.02    | 40       | 23.93    |
| Zr               | 20       | 22.90    | 15       | 17.16    | 10       | 11.43    |
| Nb               | 20       | 23.32    | 25       | 29.12    | 30       | 34.91    |
| Ta               | 10       | 22.72    | 10       | 22.69    | 10       | 22.67    |
| Fe               | 10       | 7.01     | 10       | 7.00     | 10       | 6.99     |
| Density* [g/cm³]| 8.904    | 9.034    | 9.149    |

*The theoretical density of the alloyed powder mixtures was calculated considering the densities of the elemental powders and the weight percentages.

The morphology of the initial powders is presented in figure 1 and it shows the particle shape and distribution. From these images a variety of shapes can be observed, specific for each type of elemental powder. Thus, the Ti powder consists of flattened-angular particles, for Zr they are acicular, for Nb are flaky, for Ta are irregular with a slight spheroidization tendency and for Fe are spheroidal.

The structural characterization of BIOHEA mixtures was performed on a control sample (only homogenized) and on mechanically alloyed samples. The results obtained for the homogenized sample are presented in table 2 and figure 2. It can be noted that besides Ti, Zr, Nb and Fe powders, a combination of these elements with oxygen or hydrogen appears, due to the high degree of oxidation/hydration of the metallic powders. The main compounds formed between the elemental powders are revealed by the X-ray diffraction and are presented in figure 2.

Figure 1. SEM images of elemental powders: a) Ti; b) Zr; c) Nb; d) Ta; e) Fe.
Table 2. Phases present in the BIOHEA homogenized powders.

| Compound                  | Formula       | SQ% |
|---------------------------|---------------|-----|
| Titanium                  | Ti            | 33  |
| Zirconium                 | Zr            | 8   |
| Iron                      | Fe            | 5   |
| Niobium                   | Nb            | 17  |
| Tantalum Iron Oxide       | Ta0.5Fe0.5O2  | 5   |
| Zirconium Hydride         | ZrH1.5        | 2   |
| Zirconium Hydride         | ZrH1.6        | 9   |
| Iron Zirconium Oxide      | Zr3FeO0.6     | 20  |

Figure 2. XRD patterns of the homogenized BIOHEA alloy.

The results obtained for the mixtures alloyed for 20 h are shown in table 3 and figure 3. It was observed that the formation of the NbTiZr phases is the dominant feature, and the presence of some unalloyed powders can be also seen in figure 4. The SEM image and EDAX analysis of the alloyed powders are shown in figure 4.

Table 3. Phases present in BIOHEA powders alloyed for 20 hours.

| Compound                  | Formula       | SQ% |
|---------------------------|---------------|-----|
| Niobium Titanium Zirconium| Zr0.04Ti0.71Nb| -   |
| Tantalum                  | Ta            | -   |
| Iron Zirconium            | Zr2Fe         | -   |

Figure 3. XRD pattern of BIOHEA powders alloyed for 20 hours.
It is suggested that the alloying process started but the milling time was not sufficient for a complete mixing between the powders, in order to form well-defined homogenous mixtures. This is also evidenced by the X-ray analysis result for each elemental powder, which is presented in figure 5. Thus, Ti represents 45% of the powder mix, Fe 17%, Ta 12%, Zr 4%, and the Nb content is 3%.

Figure 4. SEM image and EDAX spectrum for the BIOHEA powder alloyed for 20 h.

Figure 5. SEM images of the BIOHEA powder mixture (a) and of the elements (b) for the sample alloyed for 20 h. Mapping of each element: (c) Ti; (d) Fe; (e) Ta; (f) Zr; (g) Nb.
The maximum value of the microhardness for the TiZrNbTaFe alloy is of 955 MPa. Using the correlation between HV and the tensile strength $\sigma$: $\sigma = HV/3$, provided by Zhang et al. [32], a calculated value of $\sigma = 318$ MPa can be obtained.

The results of the corrosion tests in Ringer solution for the BIOHEA 2 sample and the Ti–6Al–4V alloy are given in figure 5.

Figure 6 shows the potentiodynamic polarization curves of the BIOHEA 2 and Ti-6Al-4V alloys in Ringer's lactate solution at 37°C. Both polarization curves show a similar variation trend and can be divided into four regions. In the first region (Region a), the current density increases with the potential increase. Both alloys exhibit a typical activation polarization and have a linear range defined between the potential and the current density in the Tafel regions. The corrosion potential ($\phi_{corr}$) and the corrosion current densities ($J_{corr}$) are obtained by extrapolation analysis of the Tafel slope using both the anodic and cathodic curves. The results show that the $\phi_{corr}$ values for the Ti-6A1-4V and BIOHEA 2 alloys are of approximately -125.5 and -71.7 mV (vs SCE), respectively. The $J_{corr}$ value of the BIOHEA 2 alloy is approximately 0.22 μA/cm², which is lower than that of the Ti6Al4V (about 0.31 μA/cm²).

![Figure 6. Anodic polarization curves for the BIOHEA 2 and Ti6Al4V alloys.](image)

The passive current density ($J_p$) of the BIOHEA 2 alloy is of approximately 8.46 μA/cm², also lower than that of Ti6Al4V (approx. 12.35 μA/cm²). After a slow increase of the current density, an increase of the potential value can be observed for both alloys in the c region, which should be attributed to the passive dissolution of chlorine ions from the solution. When the potential increases, the current densities are stabilized again in the d region, which means that the passive films turn into the re-passive state.

It is obvious that the restoration time for the passive film of the BIOHEA 2 alloy is shorter than that of the Ti6Al4V alloy. This suggests that the passive film formed on the surface of the BIOHEA 2 sample is more stable and more protective than the one formed on the Ti alloy.

It can be observed from the polarization curves that the BIOHEA 2 sample has a higher corrosion potential, a lower corrosion current density, lower and more stable passive current densities and a wider passive region, compared to the Ti-6Al-4V ELI alloy, indicating that the HEA alloy has a better corrosion resistance in the Ringer's solution media.

The corrosion resistance of metals and alloys depends on several factors, such as chemical composition, environment and microstructure. In the present work, the BIOHEA 2 alloy exhibits better corrosion resistance than Ti-6Al-4V, which can be attributed mainly to the addition of the alloying
elements (Nb, Ta and Zr), resulting in the formation of a more stable inert oxide film (composed mainly of TiO2, Nb2O5, NbO2, Ta2O5 and ZrO2) on the surface of BIOHEA 2 alloy.

According to Yu et al [33], the addition of Nb and Zr in the Ti matrix has led to the formation of a multi-component alloy with an extremely high resistance to active and passive dissolution in acids. They explained the beneficial effect of simultaneous alloying with Nb or Zr on the corrosion resistance through the formation of strong covalent bonds between the closely located Ti, Nb and Zr, through the completion of the d level of electrons [33]. The addition of Ta can improve the corrosion resistance of Ti alloys in chloride solutions because pure Ta is chloride resistant due to the relative stability of the Ta2O5 oxide film. Moreover, Ta, Zr and Nb ions have a lower solubility than Al and V ions in aqueous media [34], indicating that the passive film of the BIOHEA 2 alloy is more stable and more difficult to dissolve in the solution compared to that of the Ti-6Al-4V ELI.

The distribution of the alloying elements in different phases also influences the corrosion resistance of these two alloys to some extent. Previous studies have shown that the differences in structure and chemical composition between the α and β phases of the Ti alloys cause galvanic corrosion, leading to the formation of an unstable passive layer and the acceleration of the corrosion process [35]. He et al [36] reported that the large difference in composition between the α and β phases determines the obtaining of different rates for the formation of oxide films on the surface of the α and β phases, which results in film rupture at the α/β interfaces and the triggering of a corrosion attack. Thus, the segregation of α and β phase stabilizers in the Ti-6Al-4V alloy is most likely to cause galvanic corrosion between the phases and the preferential dissolution of the α/β interfaces. This is confirmed by previous reports stating that the localized corrosion often initiated at the α/β interface in the Ti-6Al-4V alloy [37]. By comparison, corrosion occurs at a much lower rate in the BIOHEA 2 alloy, due to the single β phase microstructure in which the alloying elements are distributed more evenly. Therefore, the corrosion resistance of the BIOHEA 2 alloy is much better than that of Ti-6Al-4V, which is currently used as a standard biomaterial, suggesting the promising potential of the TiZrNbTaFe high-entropy alloys for biomedical applications.

4. Conclusion
The paper investigated a novel high entropy alloy with for biomedical applications. Three TiZrNbTaFe alloys by powder metallurgy (PM) route and the influence of the processing parameters (milling time, compaction and sintering) on their microstructure, mechanical properties and corrosion behaviour was investigated. The results obtained for the corrosion rate were remarkable and the overall corrosion resistance of the TiZrNbTaFe HE alloys was higher than that of currently used Ti–6Al–4V alloy.

These characteristics make the studied alloys promising materials for applications in the field of biomedical devices.

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