Effect of Titanium Addition on the Structure, Microstructure, and Selected Mechanical Properties of As-Cast Zr-25Ta-xTi Alloys

Pedro Akira Bazaglia Kuroda 1,2, Barbara Leticia Tomaz Pedroso 3, Fenelon Martinho Lima Pontes 4 and Carlos Roberto Grandini 2,3,*

1 Departmento de Engenharia de Materiais, UFSCar—University Federal de São Carlos, São Carlos 13565-905, SP, Brazil; pedro.kuroda@unesp.br
2 IBTN/Br—Institute of Biomaterials, Tribocorrosion and Nanomedicine—Brazilian Branch, Bauru 17033-360, SP, Brazil
3 Laboratório de Anelasticidade e Biomateriais, UNESP—University Estadual Paulista, Bauru 17033-360, SP, Brazil; barbara.leticia@unesp.br
4 Departamento de Química, UNESP—University Estadual Paulista, Bauru 17033-360, SP, Brazil; fm.pontes@unesp.br
* Correspondence: carlos.r.grandini@unesp.br; Tel.: +55-14-31039653

Abstract: Ti alloys are the most used metallic materials in the biomedical field due to their excellent biocompatibility associated with good corrosion resistance in body fluids and relatively low elastic modulus. However, the alloys used in the orthopedic area have an elastic modulus that is 2 to 4 times higher than that of human cortical bone. Searching for new alloys for biomedical applications and with low elastic modulus, zirconium gained prominence due to its attractive properties, especially its biocompatibility. The purpose of this paper is to present novel as-cast alloys of the Zr-25Ta-xTi system and analyze the influence of titanium on the structure, microstructure, microhardness, and elastic modulus of the alloys. The alloys were prepared using an arc-melting furnace. X-ray diffraction measurements and microscopy techniques were used to characterize the crystalline structure and microstructure. From structural and microstructural characterizations, it was observed that titanium acted as an α-stabilizing element since its increase in the precipitation of the orthorhombic α” phase, an intermediate phase from β to α phases, in the alloys. Regarding microhardness measurements, the alloys have higher hardness than pure zirconium due to solid solution hardening that detaches the Zr-25Ta alloy, which has a high hardness value of the precipitation of the ω phase. Among the studied alloys, the Zr-25Ta-25Ti alloy is highlighted, demonstrating the lowest result of modulus of elasticity, which is approximately 2 times higher than the human cortical bone, but many alloys used in the biomedical field, such as pure titanium, have elastic modulus values almost 3 times higher than that of human bone.

Keywords: Zr alloys; biomaterial; microstructure; mechanical properties

1. Introduction

As technology advances and quality of life increases, the demand for metallic biomaterials for use as orthopedic and dental implants increases. In the search for new materials for biomedical applications, zirconium gained prominence [1]. Several recent studies in the literature show promising results of mechanical properties, corrosion resistance [2], and biocompatibility [3] of zirconium alloys (Zr-Ti, Zr-Nb, Zr-Mo, Zr-Ta, Zr-Zr-Nb-Zn, Zr-Mo-Zn, Zr-Nb-Ti, and Zr-Al-Fe-Nb) [4–13] or titanium alloys that have zirconium in their chemical composition (Ti-Ta-Zr, Ti-Nb-Zr-Mn, Ti-Zr-Mo, Ti-Zr-Mo-Ag, Ti-Zr-Mo-Mn, and Ti-Nb-Ta-Zr-Mo) [14–21].

Zirconium and titanium belong to the IVB group in the periodic table. They are known to have a similar structure and chemical properties [22], enabling the study of...
zirconium alloys for biomedical applications. Besides having good mechanical properties compared to stainless steel and Co-Cr alloys [23], zirconium alloys have good corrosion resistance, good biocompatibility in body fluids, and their implantation in bone tissue induces the formation of a small bone apatite layer on their surfaces [1]. Zirconium is an element that has an allotropic transformation at a temperature of 862 °C, where below this temperature, its crystalline structure is hexagonal compact (α phase). Above this temperature, its crystalline structure is body-centered cubic (phase β) [24]. Titanium undergoes an allotropic transformation similar to that of zirconium at a temperature of 883 °C [25]. Tantalum has a body-centered cubic crystal structure, a weak β-stabilizer element, and is often used to control the titanium alloys’ structure and microstructure [26].

Tsuno et al. [10] produced binary Zr-Ta alloys (Ta = 10, 20, 25, 30, 40, and 50 wt%), and the analysis of their structures and microstructures showed that, in the concentrations of 10 and 18 wt% tantalum, the alloys are of α type. With tantalum quantities in the range between 30 wt% and 50 wt%, the α and β phases coexist. Tantalum was found to act as a β-stabilizing element in zirconium alloys and produced similar results for titanium alloys [27,28].

Hsu et al. [29] studied Zr-Ti alloys. The weight percentage of titanium ranged from 10% to 40%. It showed that Zr-10Ti alloy has only the α phase as a microstructure and, with titanium contents above 20 wt%, it is already possible to visualize β phase precipitates. Moreover, the Zr-40Ti alloy has only the β phase as its crystalline structure. Hence, the results showed that the alloys’ crystalline structure depends on titanium in a solid solution.

Physical research revealed that significant microstructural refinement of titanium and zirconium alloys is observed after the impact-oscillatory loading, as the result of which the fine grains are formed not only within the very basis of the alloy, but also the process of sub grain refinement takes place within this basis [30].

To our knowledge, ternary alloys of the Zr-25Ta-xTi system never have been studied and produced. Taking advantage of Zr-Ti and Ti-Ta alloys’ qualities and potential in the biomedical field, it is expected that the ternary alloy system will have good structural, microstructural, and mechanical properties for use as a biomaterial too. This study’s objectives were to produce as-cast alloys of the Zr-25Ta-xTi system (x = 0, 15, 25, and 35 wt%) and analyze the effect of substitutional titanium on the structure, microstructure, and some selected mechanical properties of the produced alloys.

2. Materials and Methods

Leaf-shaped zirconium (99.8% purity, Aldrich), tantalum blades (99.9% purity, Goodfellow), and titanium bars (99.8% purity, Sandinox) were selected into the nominal compositions for melting. Ingot melting was performed using an arc-melting furnace with a water-cooled copper crucible, non-consumable tungsten electrode, and argon-controlled atmosphere. Applying a potential difference between the electrodes, a dielectric breakdown occurs, where the argon gas is ionized, and this beam impacts on the materials, melting the precursors [14,21,31,32].

To verify the quality and stoichiometry of the produced samples, the chemical composition of the samples was verified using an induced coupled plasma optical emission spectrometer (ICP-OES), Vista model (Varian, Mulgrave, Australia) [33] and energy dispersive spectroscopy (EDS), using a scanning electron microscope, model EVO-015 (Carl Zeiss, Jena, Germany), with an INCA probe. For gas analysis, a model TC400 gas analyzer (LECO, St. Joseph, MI, USA) was used [34], and for density determination, an Explorer model (Ohaus, Parsippany, NJ, USA) analytical balance using the Archimedes principle was employed.

The samples’ crystal structure was analyzed by the X-ray diffraction technique, using a MiniFlex 600 model (Rigaku, Tokyo, Japan) diffractometer. The X-ray source was Cu Kα radiation at a voltage and current of 40 kV and 15 mA, respectively. Measurements were made in fixed-time mode, with 0.02° of step, in the range of 20° and 80°, and a rate of
10° per min. The crystallographic sheets used to obtain crystallographic information were obtained from the Inorganic Crystal Structure Database (ICSD).

To analyze the microstructure of the produced alloys, the light microscope and scanning electron microscopy technique was used. A BX51M model (Olympus, Tokyo, Japan) microscope was used to obtain the images.

The mechanical properties were obtained by Vickers microhardness measurements using a HMV-2 model (Shimadzu, Kyoto, Japan) hardness tester, with a load of 200 g and a time of 60 s [35]. To measure the elasticity modulus, Sonelastic® equipment (ATCP, Ribeirão Preto, Brazil) based on the impulse excitation technique was used [36]. A complete set of the values of tensile strength, yield strength, and elongation of investigated alloy can be obtained in [37].

All measurements were carried out at room temperature.

3. Results and Discussion

The chemical composition results of the produced samples showed that alloys have a small quantity of metallic impurities, especially hafnium, an element found in nature together with zirconium, which makes it difficult to separate the elements (Figure 1) [24]. Hence, materials with high levels of zirconium have a higher concentration of hafnium in their chemical composition. After hafnium, nickel is the second most detected metallic impurity; nickel is derived from precursor materials. The other impurity concentrations are not significant. From Table 1, it can be concluded that the alloys were produced with good quality. The tantalum and zirconium concentrations were slightly below the nominal values established in the work. These results are expected because the impurities decrease the detection of tantalum and zirconium elements.

![Figure 1. EDS elemental mapping of Zr-25Ta (a), Zr-25Ta-15Ti (b), Zr-25Ta-25Ti (c), and Zr-25Ta-35Ti (d) alloys.](image-url)
Table 1. Chemical analysis of the produced Zr-25Ta-xTi alloys using ICP-OES.

| Element (wt %) | Zr-25Ta | Zr-25Ta-15Ti | Zr-25Ta-25Ti | Zr-25Ta-35Ti [14] |
|---------------|---------|--------------|--------------|------------------|
| Al            | 0.34    | 0.27         | 0.01         | 0.16             |
| Cr            | 0.01    | 0.01         | 0.01         | 0.01             |
| Cu            | 0.01    | 0.01         | 0.01         | 0.66             |
| Fe            | 0.41    | 0.05         | 0.09         | 0.05             |
| Hf            | 1.00    | 0.77         | 1.10         | 0.20             |
| Mo            | 0.01    | 0.11         | 0.09         | 0.01             |
| Ni            | 0.18    | 0.18         | 0.01         | 0.08             |
| Si            | 0.01    | 0.01         | 0.01         | 0.07             |
| Ta            | 21.7    | 21.64        | 23.5         | 23.5             |
| Zr            | 72.2    | 59.3         | 45.1         | 37.2             |
| Ti            | Balance | Balance      | Balance      | Balance          |

Regarding the gas analysis results, shown in Table 2, the produced alloys have a low concentration of oxygen and nitrogen gas impurities. The melting technique with the inert argon-controlled atmosphere has been satisfactorily performed since zirconium and titanium are highly reactive with oxygen. Table 3 presents the analysis of element distribution by EDS. The results have shown that the alloys have zirconium and tantalum amounts like the nominal values. These results corroborate the results obtained by ICP-OES. Furthermore, for the quantification of the elements, element distributions on the alloys' surface were performed. Figure 1 shows the mapping of the elements of the produced alloys, where the points in blue represent zirconium, points in green represent tantalum, and red points represent titanium. It is impossible to observe segregates or agglomerates of tantalum, zirconium, or titanium from the image. If the melting was not performed satisfactorily, tantalum precipitates could be observed due to their high melting point [24]. Finalizing the chemical characterization, Figure 2 shows the produced alloys' density results compared to the theoretical values. It is observed that the alloys' density is close to the theoretical values, indicating a suitable stoichiometry. The values differ slightly from the theoretical values due to metallic impurities that modify the density. Regarding titanium concentration, it was observed that the density decreases with the addition of titanium. This happens because titanium has a lower density value than zirconium; therefore, its increase in alloy decreases the concentration of zirconium, thus decreasing the density [22].

Table 2. Gas analysis of the produced Zr-25Ta-xTi alloys.

| Alloy            | O (wt %)     | N (wt %)     |
|------------------|--------------|--------------|
| Zr-25Ta          | 0.132 ± 0.004| 0.004 ± 0.001|
| Zr-25Ta-15Ti     | 0.131 ± 0.005| 0.003 ± 0.001|
| Zr-25Ta-25Ti     | 0.178 ± 0.039| 0.010 ± 0.001|
| Zr-25Ta-35Ti [14]| 0.144 ± 0.003| 0.012 ± 0.001|

Table 3. Quantitative chemical analysis of the produced Zr-25Ta-xTi alloys using EDS.

| Alloy            | Ta (wt %) | Ti (wt %) |
|------------------|-----------|-----------|
| Zr-25Ta          | 28.6      | –         |
| Zr-25Ta-15Ti     | 27.6      | 14.7      |
| Zr-25Ta-25Ti     | 25.8      | 24.5      |
| Zr-25Ta-35Ti     | 26.9      | 35.7      |
The X-ray diffraction results (Figure 3) indicate that the Zr-25Ta alloy has a body-centered cubic crystalline structure (β phase) and a tetragonal crystalline structure (ω phase). Due to the presence of the ω phase, this alloy must have high hardness and modulus of elasticity values, making it difficult to use it after melting for biomedical applications. For Zr-25Ta-15Ti and Zr-25Ta-25Ti alloys, only β phase peaks can be observed. With the addition of 35 wt% of titanium, a small peak of the orthorhombic α” phase is observed at approximately 42°. In general, titanium acted as an α-stabilizer element in titanium alloys [38], since its addition resulted in the nucleation of phase α”, which is intermediate from β to α phases. With these results, it is expected that alloys with higher titanium contents will have martensitic phases in their structures and microstructures. These results differ from Hsu et al. [29], where the addition of titanium in the Zr-Ti system induces precipitation of the β phase. In this present paper, the addition of titanium induces martensitic phases besides the β phase. This characteristic difference must be related to the presence of tantalum, which acts as a β stabilizer. From the literature, we know that the Ti-25Ta alloy, after the solution treatment, is a single-phase alloy with an orthorhombic structure α” [39]. Thus, titanium in the Zr-25Ta system suppresses the β phase.

Regarding the microscopy images, Figure 4 shows the optical (left) and scanning electron (right) micrographs, for the Zr-25Ta (Figure 4a), Zr-25Ta-15Ti (Figure 4b), Zr-25Ta-25Ti (Figure 4c), and Zr-25Ta-35Ti (Figure 4d) alloys, respectively. It is possible to observe and visualize the grain boundaries on the alloys’ surface and a β phase matrix for alloys in the Zr-25Ta-xTi system [38]. However, in Figure 4d, which shows the micrographs of the Zr-25Ta-35Ti alloy, it is possible to observe small α-orthorhombic phase precipitates [40]. These precipitates are needles in localized intra-grain.

Comparing the obtained results using X-ray diffraction and microscopy techniques to analyze the structure and microstructure, both techniques corroborate them. The Zr-25Ta alloy is of β and ω phases type, remembering that the ω phase is only detected via the technique of transmission electron microscopy [41]. Zr-25Ta-15Ti and Zr-25Ta-25Ti alloys are β-type alloys, and the Zr-25Ta-35Ti alloy is a metastable β alloy with α” phase.
alloys with 25 and 35 wt % of titanium, there was a decrease in the microhardness value. This decay is related to the loss of $\beta$ phase stabilization due to titanium acting as an $\alpha$-stabilizer element [43].

The mechanical property measurements are shown in Figure 5 (Vickers microhardness) and Figure 6 (elastic modulus). Analyzing the results presented in Figure 5, it can be observed that the alloy without the presence of titanium had a high hardness of 500 HV. This high hardness value is related to the presence of the $\omega$ phase, which is undesirable in biomedical alloys as it makes the material hard and brittle [42]. With the addition of 15 wt % of titanium, there was a suppression of the $\omega$ phase, reducing the alloy’s hardness. For alloys with 25 and 35 wt % of titanium, there was a decrease in the microhardness value. This decay is related to the loss of $\beta$ phase stabilization due to titanium acting as an $\alpha$-stabilizer element [43].
In the results for the modulus of elasticity, shown in Figure 6, it is observed that the addition of titanium changed the elastic modulus of the alloys in a similar way to the hardness. The Zr-25Ta alloy has a high elastic modulus value due to the presence of the ω phase [44] but smaller than the cp-Ti and the Ti-6Al-4V alloy [23]. In the Zr25Ta-15Ti alloy, there was a decrease in the modulus of elasticity value since the alloy has only the β phase as a crystalline structure. With the addition of 25 wt% of titanium, the Zr-25Ta-25Ti alloy has an excellent modulus value of 60 GPa, the lowest value of the system. This alloy has only the β phase in its microstructure, as titanium is an α-stabilizing element. The increase
of titanium modifies the atomic interaction forces of the $\beta$ phase, which becomes weak due to lower $\beta$ phase stability, decreasing the modulus of elasticity $[45,46]$. For the Zr-25Ta-35Ti alloy, there is an increase in the modulus value because the alloys are biphasic or even three-phased. There is evidence of precipitation of a small fraction of the omega phase that tends to increase the modulus of elasticity (probably dissolved in the beta matrix, making it difficult to detect by the used XRD equipment $[47]$). The studied alloys have excellent modulus of elasticity values. The alloys have better results than many orthopedic and dental implant alloys, such as cp-Ti, cp-Ta, Ti-6Al-4V, Ti-15Mo, Co-Cr alloys, and stainless steel, among others $[23]$. Figure 7 shows a comparison of the elastic modulus values of the alloys developed in this work compared to commercial alloys and titanium alloys commonly used in the biomedical field. However, more mechanical characterization tests are needed to analyze its viability as a biomaterial, in addition to biocompatibility analysis.

Figure 5. Vickers microhardness as a function of titanium concentration for all Zr-25Ta-xTi alloys used in this study.

Figure 6. Elastic modulus as a titanium concentration function for all Zr-25Ta-xTi alloys used in this study.
Figure 7. Young’s modulus of Zr-25Ta-xTi alloys analyzed in this paper, compared with commercial metals used as biomaterials (reprinted with permission from reference [23]).

4. Conclusions

From the results presented in this paper, it is possible to conclude that:

Chemical composition and EDS mapping measurements indicate that the produced alloys are homogeneous and preserve the proposed stoichiometry;

Structural and microstructural analyses show that titanium acted as an α-stabilizing element because its addition to the alloys of the Zr-25Ta-xTi system precipitates the formation of phase α'' in some β-type alloys;

Zr-25Ta alloy has the ω phase in its structure, making it difficult to use as a biomaterial. The alloy has high hardness and elastic modulus values compared to the other alloys in the system. Even demonstrating the worst results of the system, this alloy still has better results than many alloys used as biomaterials, such as cp-Ti, Ti-6Al-4V, Co-Cr alloys, and stainless steel, among others;

The microhardness and modulus of elasticity tend to decrease with the addition of titanium; this is due to the lower stabilization of the β phase with titanium. Only for the Zr-25Ta-35Ti alloy, there was a slight increase in modulus value because the alloy has two phases as a microstructure, which makes the dislocations motion difficult and thus increases the alloy’s modulus of elasticity;

Zr-25Ta-25Ti is the best alloy in this study. It has low hardness and the lowest elasticity modulus value (60 GPa) and is only twice as high as cortical bone. However, more mechanical characterization tests are needed to analyze its viability as a biomaterial, in addition to biocompatibility analysis.

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