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Effects of the chemical composition on the microstructural characteristics of Ti-Nb-Ta-Zr alloys

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Abstract. Among the biomedical alloys, titanium based alloys are currently the best solution for implantation as a result of their low levels of toxicity. To improve mechanical properties, a series of chemical compositions of some titanium alloys have been studied over the past 15 years, to provide elasticity values as close as possible to bone. The paper presents the main mechanical and microstructural characteristics of Ti-Nb-Ta-Zr alloys compared to other titanium brands. It was found that in the absence of heat treatments, the highest hardness values (437HV1) were obtained for the Ti15Nb7.6Ta8Zr alloy, and the lowest hardness value (259 HV1) was obtained for the Ti98.4 alloy.

1. Introduction

Titanium is used as a biomaterial because it has excellent specific strength and corrosion resistance, no allergy-related problems and the best biocompatibility among metallic biomaterials [1-16]. Titanium's lightness and good mechano-chemical properties are salient features for implant applications [2]. Pure titanium or the Ti-6Al-4V alloy is still the most widely used for biomedical applications among the biomaterials. For instance, the biocompatibility of the Ti6Al4V alloy has since been called into question due to reports that the gradual release of aluminium, and particularly vanadium ions, from the surface of alloy can cause local adverse tissue reactions and immunological responses [1, 3 and 4].

Therefore, the developments of titanium alloys targeted for biomedical application are highly required. Recently, the mechanical biocompatibility of biomaterials has been regarded as an important factor, and therefore the research and development of β types of titanium alloys, which are advantageous from this point of view, have been on an increase [1]. The β type titanium alloys show excellent cold workability and high strength. The strength of β type titanium alloys can be increased while keeping Young's modulus low by cold working after solution treatment even the elongation and reduction area are a little lowered at low cold work ratio by around 20% [1]. A low Young's modulus equivalent to that of a cortical bone is simultaneously required in order to inhibit bone absorption into the implant [5, 6 and 7].

The elements which are considered to be non-toxic and non-allergenic through the reported data of cell viability for pure metals, polarization resistance and tissue compatibility, which can be used as alloying elements, are: Nb, Ta, Zr, Sn, Mo, Fe and Hf. The stabilisation of titanium alloys using different alloying elements, for the α-phase (e.g. Al, O) and for the β-phase (V, Fe, Mn, Nb, Ta), is a current practice. For a content of more 5wt% aluminium, the precipitation of Ti_3Al in the α_2-phase begins, as can be seen from the quasi-binary section in the ternary phase diagram of Ti6Al4V. The α_2-phase provides an extremely high hardening effect, so that the aluminium content in titanium alloys must be limited to a maximum value of 8% [8]. Furthermore, the grain size of as cast titanium alloys decreases significantly with boron addition [9]. The alloying with chemical elements such as Ta, Nb, Zr, V or Al [10, 12] leads to a change in the phase proportion and, implicitly, to a change in the mechanical and microstructural characteristics. At the same time, the rapid cooling after applying heat treatments or after welding [12-14] may cause substantial changes in the microstructural or hardness characteristics.

The paper presents some microstructural characteristics of some Ti-Nb-Ta-Zr alloys obtained by electric arc melting in a VAR ABJ furnace, under argon protection. To illustrate the effects of the alloying elements, 3 types of alloys were produced: Ti-9Nb-8Zr, Ti-14Nb-4.6Ta-4.5Zr and Ti-10Nb-7.6Ta-8Zr. The microstructure of the experimental alloys was analysed using optical and electronic scanning microscopy, chemical composition tests were performed on micro-zones and the micro-hardness was measured. It was found that the addition of the Zr, Ta and Nb alloying elements contributes to changing the hardness of the titanium metallic matrix (increase up to 437HV1) compared to unalloyed titanium (259HV1) or the Ti9Al3.6V alloy (354HV1).

2. Experimental

2.1 Materials

The experimental Ti alloys were obtained by electric arc melting in a VAR MRF ABJ 900 furnace, in an inert argon atmosphere. The samples obtained were re-melted at least 3 times on each side to ensure homogeneity and to allow the dissolution of the refractory materials Three experimental alloys were obtained by adding Nb, Zr and Ta in the metallic matrix produced by melting the titanium sponge and a Ti9Al3.6V alloy, to compare the microstructural characteristics. The coding and chemical compositions of the alloys analysed in the paper, determined by EDS analyses are shown in Table 1.

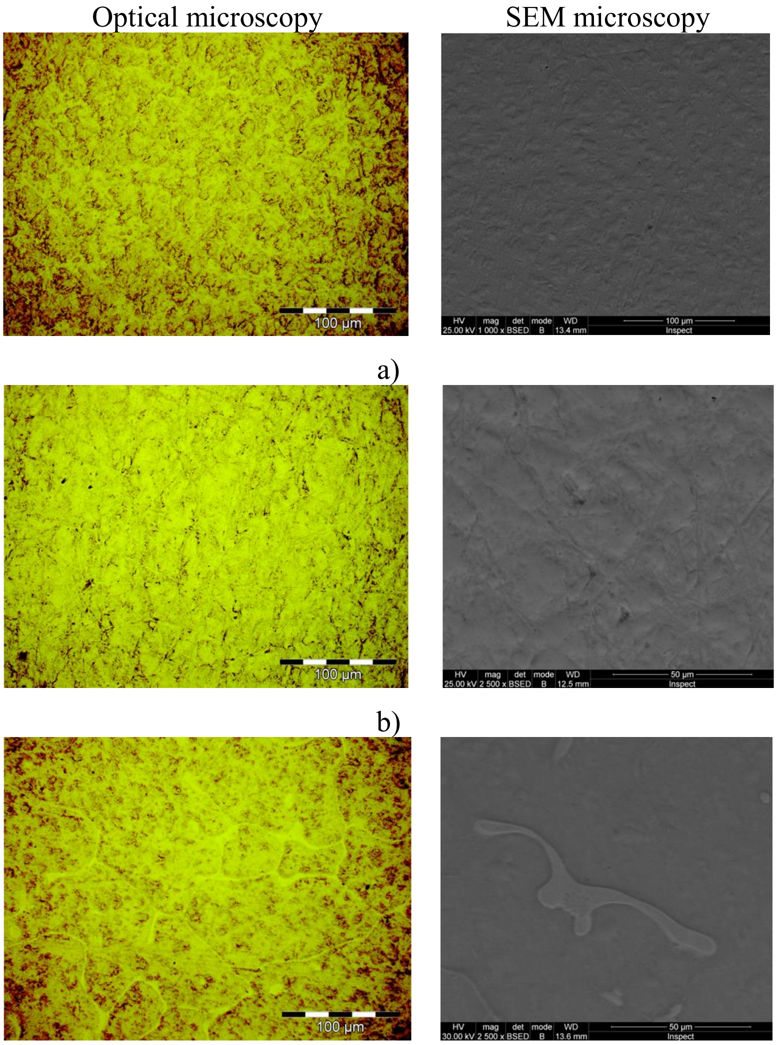
Table 1. Average chemical composition of experimental titanium alloys.

Chemical elements, %wt	**Ti1**	**Ti2**	**Ti3**	**Ti9Al3.6V**
Ti	82.74	76.79	74.40	87.3
Zr	8	4.53	8	-
Nb	9.26	14	10	-
Ta	-	4.68	7.6	-
Al	-	-	-	9.1
V	-	-	-	3.6

Table 1 shows that the Ti_3 alloy contains, in addition to the Ti_1 alloy, about 7.6 wt% Ta, while the proportions of the other 2 alloying elements (Nb, Zr) are similar. All three alloying elements were used in the Ti_2 alloy, but in varying proportions, the percentage of Nb was increased to about 14wt% and the percentage of Ta and Zr was decreased (to about 4.5wt%). It is known that Ta and Nb are chemical elements that stabilize the β phase in titanium alloys, while Zr is considered a neutral element. It is also known that the mechanical properties of the bi-phase titanium alloys ($\alpha + \beta$) are very sensitive to the morphology and geometric arrangement of the 2 phases [11]. The entirely lamellar microstructure provides increased resistance to fatigue crack propagation and better tenacity.

2.2 Microstructure

The microstructure of the experimental alloys reflects the effects of adding the alloying elements in different proportions. Thus, the Ti1 (Ti-9Nb-8Zr) alloy exhibits a homogeneous microstructure, with dendritic appearance (Figure 1a). The ternary Ti-Nb-Zr system is composed of solution phases only: liquid, β (BCC A2), and α (HCP A3) [15, 16]. The addition of tantalum in the Ti-Nb-Zr alloy does not generate substantial structural modifications (Figure 1b), but only aspects related to the morphology of the phases, which go from globulised forms to lenticular forms. The increase in the Zr and Ta content (they're almost doubling) for the Ti-10Nb-7.6Ta-8Zr alloy results in lenticular separations of the Ti-Zr and Ti-Nb phases located in the inter-dendritic areas.



a)

b)

c)

Figure 1. Microstructure of experimental titanium alloys. a) Ti-9Nb-8Zr alloy; b) Ti-14Nb-4.6Ta-4.5Zr alloy; c) Ti-10Nb-7.6Ta-8Zr alloy.

EDS analyses on micro-zones revealed the formation of phases rich in Zr (about 26 wt% Zr) and in Nb (about 15.5 wt% Nb) in the form of elongated islands placed interdendritically (Figure 2).

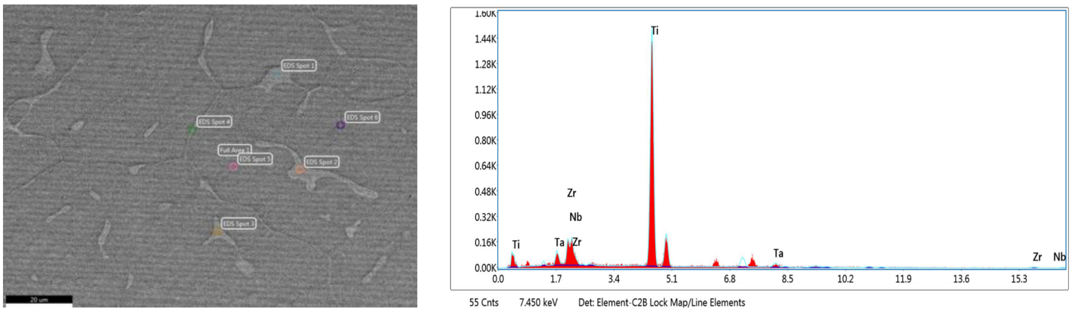


Figure 2. EDS analyses on micro-zones for sample Ti3.

2.3 Microhardness

The microhardness of the titanium alloy samples was determined using the Shimadzu HMV 2T microhardness tester, at a 1 N pressing force and a measurement time of 10 seconds. The mean microhardness values are shown in Table 2.

Table 2. Microhardness values for experimental titanium alloys.

Chemical elements, %wt	Ti1	Ti2	Ti3	Ti9Al3.6V
Average, HV1	360	319	437	354
Standard deviation, %	8.89	5.68	5.41	4.21
Coefficient of variation, %	2.49	1.78	1.24	1.19

The analysis of the microhardness values measured on the 4 types of titanium alloy samples reveals that the highest hardness was obtained for the Ti3 alloy, where the Ta and Zr percentages are the highest. The studies performed on binary titanium alloys, alloyed with Zr, Ta or Nb, have shown that the hardening and growth effects of the Young's modulus are different, as follows:

- an increase in the Young's modulus up to about 125 GPa is obtained in case of alloying with up to 50 wt% Zr;
- the alloying with 25 wt% Nb results in a Young's modulus increases to 60 GPa;
- the Young's modulus growth is continuous as the Ta percentage increases, the maximum value being of about 180 GPa [15].

3. Conclusions

Titanium alloys can be hardened by alloying with bio-compatible elements, such as Zr, Nb and Ta. The highest microhardness values were obtained in case of simultaneous alloying with the three elements mentioned, i.e. for the Ti-10Nb-7.6Ta-8Zr alloy.

The microstructure suffers changes in the morphology and phase distribution depending on the degree of alloying with Nb, Zr or Ta. By increasing the proportion of Zr and Nb, there is a separation from the solid BCC solution of Zr and Nb-rich compounds, with the formation of elongated islands on the interdendritic areas.

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