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Original Article

Effect of the substitutional elements on the microstructure of the Ti-15Mo-Zr and Ti-15Zr-Mo systems alloys☆

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ABSTRACT

Titanium alloys have excellent biocompatibility, and combined with their low elastic modulus, become more efficient when applied in orthopedic prostheses. Samples of Ti-15Mo-Zr and Ti-15Zr-Mo system alloys were prepared using an arc-melting furnace with argon atmosphere. The chemical quantitative analysis was performed using an optical emission spectrometer with inductively coupled plasma and thermal conductivity difference. The X-ray diffractograms, allied with optical microscopy, revealed the structure and microstructure of the samples. The mechanical analysis was evaluated by Vickers microhardness measurements. The structure and microstructure of alloys were sensitive to molybdenum and zirconium concentration, presenting α', α'' and β phases. Molybdenum proved to have greater β-stabilizer action than zirconium. Microhardness was changed with addition of molybdenum and zirconium, having Ti-15Zr-10Mo (436 ± 2 HV) and Ti-15Mo-10Zr (378 ± 4 HV) the highest values in each system.

1. Introduction

The development of new biomaterials is an interdisciplinary effort that often requires a collaborative effort among doctors, researchers, and engineers. The implant, in addition to not causing rejection, must possess favorable mechanical properties and preferably be bioactive, namely, stimulate cell regeneration around the implant [1].

Due to the excellent biocompatibility, corrosion resistance, and lower modulus to steels, titanium alloys have better surgical response in the case of dental and orthopedic implants.

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However, from an economic perspective, titanium alloys have disadvantages due to costly processing in relation to steels [2,3].

The most-used titanium alloy in biological applications is Ti-6Al-4V (wt%) [3], however, there are reports that vanadium causes cytotoxic effects and adverse reactions in some tissues [4], while aluminum has been associated with neurological disorders [5]. In this sense, there is a need to search for alloys with better mechanical properties and biocompatibility, and the most promising are those that have niobium, zirconium, tantalum, and molybdenum as alloying elements [3]. The titanium alloys with β structure (metastable or stable) are titanium alloys with high mechanical strength, good conformability, and high ductility. β titanium alloys also offer the unique possibility of combining low modulus of elasticity and high corrosion resistance [6].

Molybdenum is a silvery metal, very hard, and more ductile than tungsten. It has a high modulus of elasticity, and has melting points lower only than tungsten and tantalum. It is a valuable alloy agent because it contributes to the hardening and toughness of steels. It also improves the strength of steel at high temperatures [7].

Zirconium is a neutral alloying element, does not alter the allotropic transition temperature of titanium, and is thus used as a hardening agent. Besides having complete solid solubility, zirconium has chemical and physical properties similar to titanium. The addition of this element causes increased resistance to corrosion; the alloy improves the biocompatibility and leads to a decrease in melting point [8,9].

Among the studied alloys, those belonging to the system, Ti-Mo and Ti-Zr have advantageous properties such as tensile strength that is superior to pure titanium, low density, and good biocompatibility, and thus have potential for application in dental and orthopedic areas [7,10–13]. Molybdenum above 15 wt% is a beta stabilizer, and titanium alloys with a predominance of this phase have low elasticity modules compared to predominantly alpha alloys [7].

The purpose of this study is to analyze the effect of molybdenum and zirconium substitutional elements on the structure and microstructure of the Ti-15Mo-xZr and Ti-xMo-15Zr ($x = 5$, 10 and 15 wt%) systems alloys.

2. Methods

The samples used are alloys of Ti-15Mo-Zr system (TMZ) — with zirconium contents in the range of 5, 10, and 15 wt% — and Ti-15Zr-Mo system (TZM) — with molybdenum contents in the range of 5, 10, and 15 wt%. The ingots were prepared through arc-melting with a non-consumable tungsten electrode, where the raw materials were melted in a water-cooled copper crucible in an argon atmosphere to avoid possible contamination. After melting, the samples were subject to qualitative and quantitative chemical analysis of elements by plasma emission spectrometry (ICP OES), and the concentration of interstitial elements present in the sample was obtained using a gas analyzer LECO, TC-400 model. The density measurements were performed using the Archimedes' principle in an Ohaus analytical balance (0.0001 g precision).

Structural characterization was performed by means of X-ray diffraction measurements (XRD), obtained in a Rigaku model D/Max 2100/PC diffractometer, with Cu-K_α radiation of 1.544 Å wavelength. Data were collected using the powder method (taken by mechanical abrasion), with steps of 0.02°, ranging between 10° and 100°, and in fixed time of 3.2 s. Microstructural characterization was performed by optical microscopy (OM), with the measurements being carried out using an Olympus BX51M microscope. The cylindrical samples were prepared by a standard metallographic process, by polishing the samples in SiC waterproof papers until #1500 grit and colloidal alumina suspension. The chemical etching was made with H_2O, HNO_3 and HF in 85:10:5 proportion during 15 s.

Microhardness tests were performed in a Shimadzu HMV-2 model microdurometer with a load of 1.961 N for 60 s. Five measurements were carried out, and the reproducibility was very good.

3. Results and discussion

Tables 1 and 2 present the results of the chemical composition of the TMZ and TZM alloy samples, respectively. The concentrations of molybdenum and zirconium remained close to the nominal values, with metallic impurities showing non-significant quantities, and the levels of interstitial gases (oxygen and nitrogen) showing small concentrations [14].

Fig. 1 shows the values of density, compared with the theoretical value obtained from the weighted average of the main elements that compose the alloy. The density of the alloys had a gradual increase according to the increase in concentration of molybdenum (TZM system) and zirconium (TMZ system). The increase in the density of alloys occurs due to the higher density of zirconium (6.51 g/cm^3) and molybdenum (10.22 g/cm^3) compared to titanium (4.51 g/cm^3) [15]. In addition, the values were close to the theoretical values, stating the correct stoichiometry of alloys. The analysis of chemical composition and density attest the good quality of the materials used in this study.

Table 1 – Chemical composition Ti-15Mo-xZr alloys.

Element (wt%)	Ti-15Mo	Ti-15Mo-5Zr	Ti-15Mo-10Zr	Ti-15Mo-15Zr
Ti	Balance	Balance	Balance	Balance
Mo	14.47	15.01	14.77	15.20
Zr	<0.001	5.23	9.82	14.79
Al, Cr, Cu, Ni, Fe	<0.1	<0.1	<0.1	<0.1
O	0.17	0.19	0.18	0.16
N	0.01	0.04	0.03	0.06

Table 2 – Chemical composition Ti-15Zr-xMo alloys.

Element (wt%)	Ti-15Zr	Ti-15Zr-5Mo	Ti-15Zr-10Mo	Ti-15Zr-15Mo
Ti	Balance	Balance	Balance	Balance
Zr	15.60	15.13	15.59	14.80
Mo	<0.001	4.82	10.30	14.25
Al, Cr, Cu, Ni, Fe	<0.1	<0.1	<0.1	<0.1
O	0.20	0.22	0.23	0.30
N	0.02	0.04	0.04	0.03

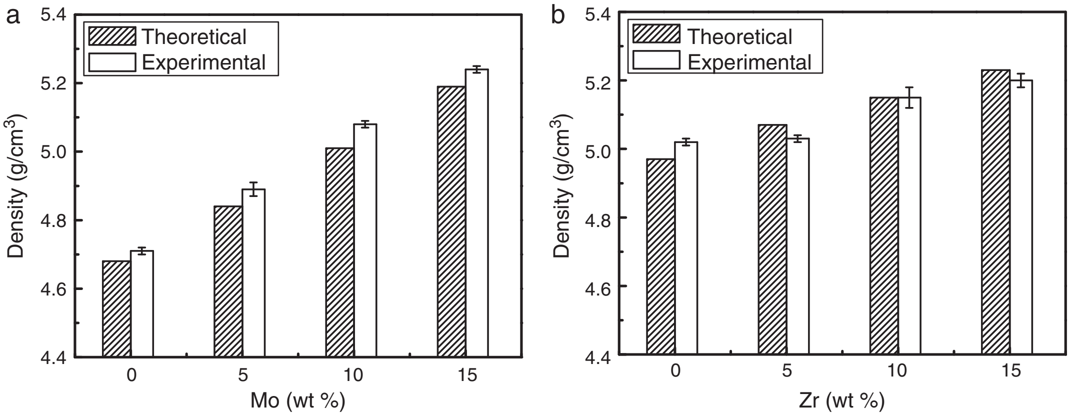


Fig. 1 – Density for samples of the Ti-15Mo-xZr (a) and Ti-15Zr-xMo (b) systems alloys.

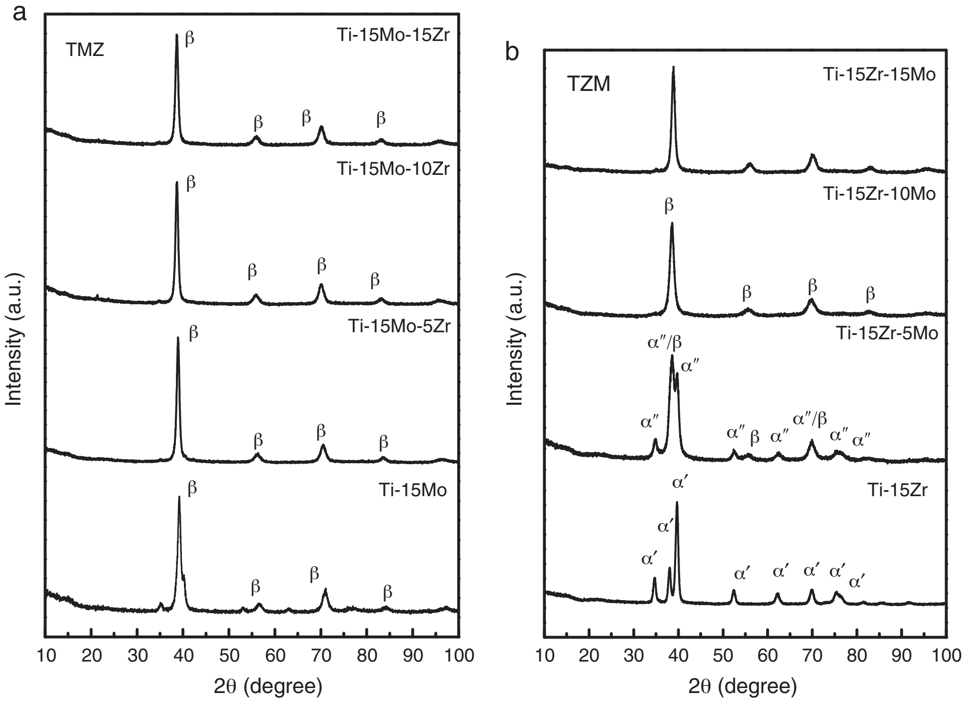
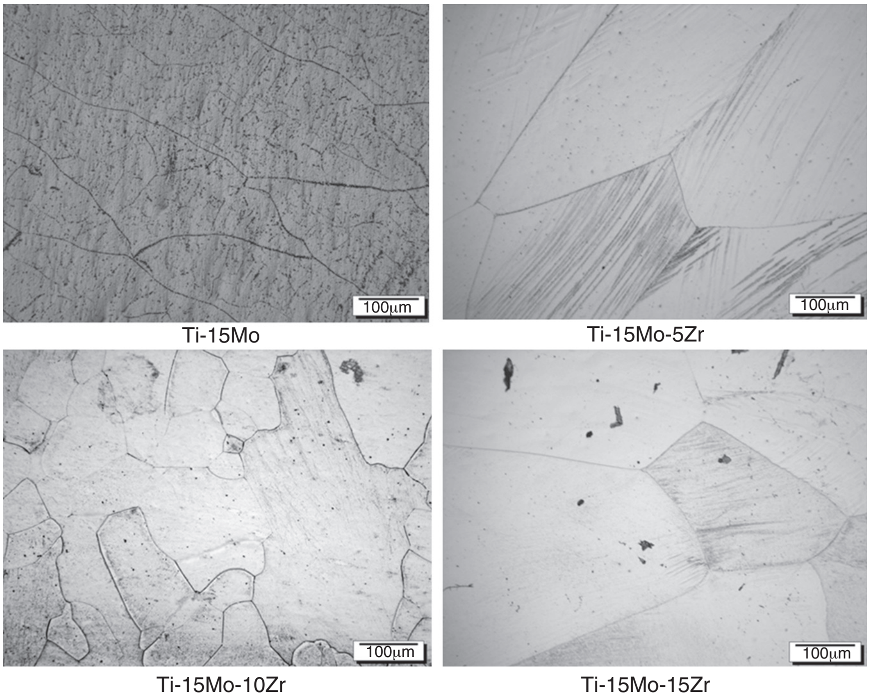


Fig. 2 – XRD patterns for samples of the Ti-15Mo-xZr (a) and Ti-15Zr-xMo (b) systems alloys.

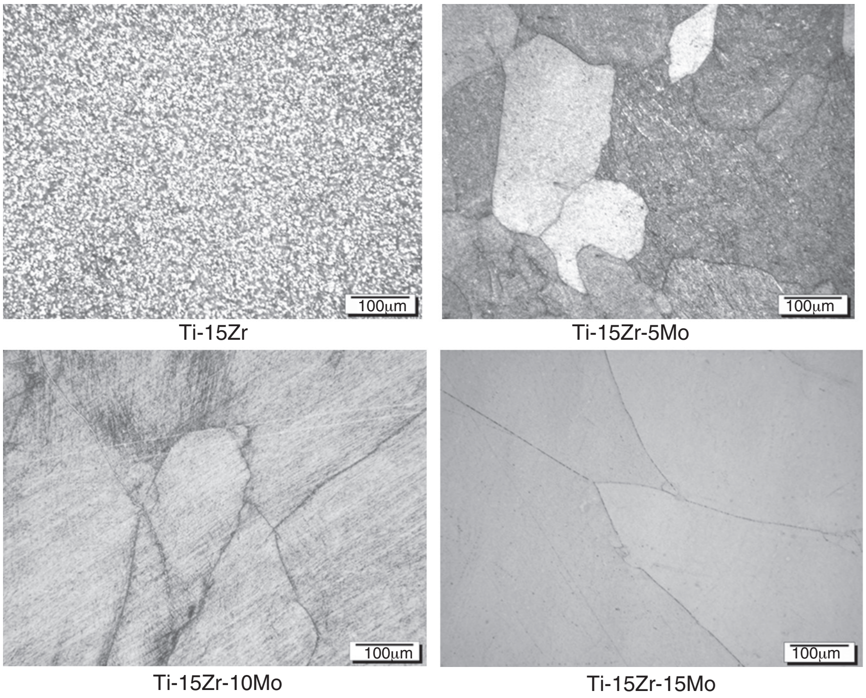
Fig. 2 shows the X-ray diffractograms of the studied alloys. In the case of the TMZ system (part (a) of Fig. 2), Ti-15Zr-5Mo alloy presented a two-phase structure, with peaks related to α″ martensitic phase (orthorhombic crystalline structure) and β phase (body centered, cubic crystalline structure). The other alloys showed a predominant pattern of β phase [16]. Only the presence of the β phase can be observed for this system due to the high concentration of molybdenum, which can decrease the β-transus temperature to below room temperature [11,17]. For the TZM system (part (b) of Fig. 2), Ti-15Zr alloy presented the same diffraction pattern as the hexagonal structure of titanium (α phase). However, the peaks are displaced to low angles, indicating a crystalline lattice deformation characteristic of α' martensite phase [13,18]. The results clearly indicate the β-stabilizer action of alloying elements in solid solution. Molybdenum is known to be a strong β-stabilizer and may retain the β phase of metastable form with 10 wt% [7,10]. Zirconium is a neutral element, but may present a slight action β-stabilizer when in solid solution with other β-stabilizers [19,20]. Binary alloys of Ti-Mo have been widely studied in the literature, and the α''/β limit is around 9 wt% as-cast condition [7,21]. The results indicated the presence of the β phase in Ti-15Zr-5Mo, which proves the action of β-stabilizer of zirconium in solid solution.

Fig. 3 presents the micrographs of the alloys of the TMZ system, where dark regions and spots resembling pitting



Ti-15Mo Ti-15Mo-5Zr
Ti-15Mo-10Zr Ti-15Mo-15Zr

Fig. 3 – Optical micrographs of Ti-15Mo-xZr alloys.



Ti-15Zr Ti-15Zr-5Mo
Ti-15Zr-10Mo Ti-15Zr-15Mo

Fig. 4 – Optical micrographs of Ti-15Zr-xMo alloys.

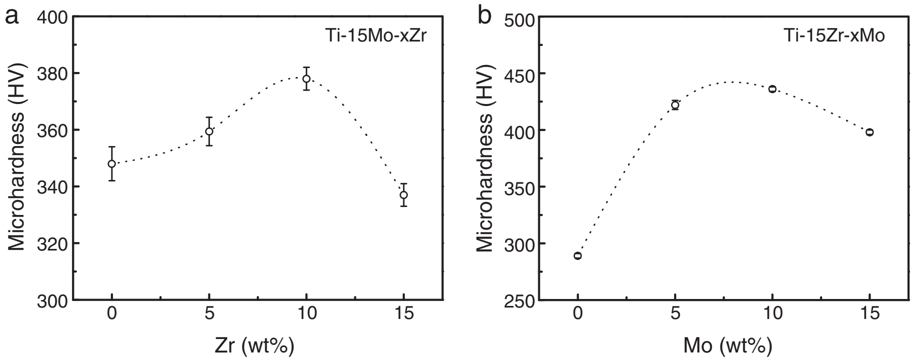


Fig. 5 – Density for samples of the Ti-15Mo-xZr (a) and Ti-15Zr-xMo (b) systems alloys.

corrosion can be observed. Corrosion of this type occurs in chemical etching of polished surfaces, being favored by internal tensions on the surface, creating regions where chemical kinetics of the reaction is accelerated. The predominance of grains of the β phase, with the absence of acicular structures concerning α′ and α″ phases, can also be seen [22].

In Fig. 4 the optical micrographs for the alloys of TZM system are presented, where it can be observed that the Ti-15Zr alloys presented a microstructure consisting of small acicular formations, characteristic of martensite α′ phase [18]. The Ti-15Zr-5Mo alloy presented irregular grains of β phase with the formation of fine needles of martensite α″ phase along and throughout an intragranular region. The Ti-15Zr-10Mo alloy presented the sharpest grain formation of β phase, with small dark precipitates of α″ phase around the grain boundaries, indicating the possibility of formation of metastable β phase type. The Ti-15Zr-15Mo alloy presented only equiaxial grain formation of β phase [12].

The micrographs corroborate the X-ray diffractograms, indicating the action β-stabilizer of alloying elements. The residual stress and the air-cooling after melting may also have influenced the microstructure of alloys resulting in irregular formats [23].

Fig. 5 presents the values of hardness for the alloys of TMZ and TZM systems in the function of zirconium (part (a)) and molybdenum (part (b)) concentration. The hardness of the alloys remained above the value of grade 2 cp-Ti (187 ± 5 HV) [15], due to solid solution hardening of alloying elements [20] along with a non-linear behavior. This nonlinear behavior of the hardness with increased molybdenum content is derived from the phase precipitation hardening [12].

For the TMZ system, addition of zirconium in solid solution favored the formation of α′ martensitic structure, with its gradual addition causing an increase in the value of hardness due to variation of the lattice parameter, which hampers the movement of dislocations [24]. It has not been possible to observe the clear presence of ω phase in the alloys, possibly because of inhibition of their formation by the addition of zirconium. The presence of ω phase may result in increased hardness and modulus of elasticity of the material, as well as contributing to their softening. The addition of zirconium on Ti-15Mo becomes effective for inhibiting the formation of ω phase [25]. In X-ray diffractograms and micrographs, it was not possible to identify the ω phase in any concentration.

In the TZM system, zirconium addition in the system favors the formation of martensite α′ structure, thus its gradual addition increases the hardness of the alloy. Thus, it would be natural that the Ti-15Mo-15Zr alloy presented the highest hardness, but it did not occur. Probably, there is a complete inhibition of the formation of the metastable ω phase in Ti-15Mo-15Zr. In addition, the formation of α″ and β phases also contribute to variations in hardness values, as observed in Ti-Nb alloys [26], Ti-Ta [27] and Ti-Mo [7].

Alloys common to the two systems (Ti-15Mo-15Zr and Ti-15Zr-15Mo) have different values regarding the hardness, despite having the same nominal composition. This fact is due to thermo-mechanical processing and the difference in the gas concentration of the alloys, which cause internal stresses that are responsible for major changes in the mechanical properties [13].

4. Conclusions

From the presented results, it can be concluded that:

- Zirconium and molybdenum alloying elements presented influence to the structure and microstructure of alloys, through the β-stabilizer action;
- Molybdenum proved to have greater β-stabilizer action than zirconium;
- Hardness showed a nonlinear behavior with the concentration of molybdenum and zirconium, due to concentration of these alloying elements in the crystalline alloy and phase precipitation;
- Ti-15Mo-15Zr presented the best potential for a possible biomedical application due to adequate combination of β-phase and the mechanical properties.

Conflicts of interest

The authors declare no conflicts of interest.

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