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Processing and properties of Ti-15Zr-15Mo-(1-3)Ag alloys for applications as biofunctional materials

Processamento e propriedades das ligas Ti-15Zr-15Mo-(1-3)Ag para aplicações como materiais biofuncionais

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ABSTRACT

Titanium (Ti) is employed as a biomaterial because of its superior biocompatibility and favorable mechanical properties that can be changed with the addition of alloying elements, such as zirconium and molybdenum. Silver is an alloying element recognized for its antibacterial action, which can improve the mechanical strength and decrease Young's modulus of Ti. This work studies the effect of silver addition (1 and 3 wt%) on the crystalline structure, microstructure, Vickers microhardness and Young's modulus of Ti-15Zr-15Mo (wt%) alloy, targeting for a potential application as a biofunctional material. The ingots were produced by argon arc melting and subsequently subjected to a heat treatment of homogenization, hot-rolling and solubilization heat treatment. Chemical composition indicated good quality on the processing of the alloy. Crystalline structure and microstructure analyzed by X-ray diffraction, optical microscopy and scanning electron microscopy showed only titanium's β phase. Finally, mechanical properties studied by Vickers microhardness and Young's modulus measurements presented that the addition of low content of silver did not significantly modify the alloy's mechanical properties, but it can include antibacterial properties on the bulk.

KEYWORDS: Biomaterial, Titanium alloys, Silver.

RESUMO

O titânio (Ti) é empregado como biomaterial por causa da sua alta biocompatibilidade e das propriedades mecânicas favoráveis que podem ser ainda alteradas com a adição de elementos de liga, como zircônio e molibdênio. A prata é um elemento de liga reconhecido por sua ação antibacteriana, que pode melhorar a resistência mecânica e diminuir o módulo de elasticidade do Ti. Este trabalho estuda o efeito da adição de prata (1 e 3 %p) na estrutura cristalina, microestrutura, microdureza Vickers e módulo de elasticidade da liga Ti-15Zr-15Mo (%p), visando à potencial aplicação como material biofuncional. Os lingotes foram produzidos por fusão a arco voltaico em atmosfera de argônio e posteriormente submetidos a um tratamento térmico de homogeneização, laminação a quente e tratamento térmico de solubilização. A composição química indicou boa qualidade no processamento da liga. A estrutura cristalina e a microestrutura analisadas por difração de raios x, microscopia óptica e microscopia eletrônica de varredura mostraram apenas a fase β do titânio. Finalmente, as propriedades mecânicas estudadas por medidas de microdureza Vickers e módulo de elasticidade mostraram que a adição de baixo teor de prata não modificou significativamente as propriedades mecânicas da liga, mas pode incluir propriedades antibacterianas no material.

PALAVRAS-CHAVE: Biomateriais, Ligas de titânio, Prata.

INTRODUCTION

Biomedical researches have been sought an enhancement of the global quality of life. In this scenery, biocompatible metallic materials are constantly focused on investigation, e.g., titanium (Ti), niobium, molybdenum (Mo), zirconium (Zr), and tantalum (Ta)[1-5]. These metallic materials are mainly employed in surgical implants, as orthopedical, dental and cardiovascular implants[6]. The main commercial materials are stainless steel, Co-Cr-Mo alloys and Ti-based alloys, such as Ti-6Al-4V[7]. Ti has biocompatibility and an excellent corrosion resistance. However, their mechanical properties still need to be improved[8]. Nowadays, it is sought the development of novel Ti alloys, with enhanced mechanical properties, corrosion resistance, and better compatibility with the bone tissues.

In natural conditions, Ti presents an allotropic transformation around 882.5ºC (1,155.5 K), changing its crystalline structure from hexagonal close-packed (hcp, α phase) to body-centered cubic (bcc, β phase). However, this temperature can be decreased with the addition of alloying elements such as Zr and Mo, which exhibit β-stabilizing action[9]. This phase transformation turns possible controlling of its mechanical properties by means of heat treatments and mechanical processing. Distinct processing routes can significantly impact the mechanical properties and microstructure of Ti-based alloys[10].

As well as Ti, Zr and Mo can present good mechanical and corrosion strength, in addition to high biocompatibility. Thus, the development of Ti-Zr-Mo system alloys combined novel β-type Ti alloys with low Young's modulus[11,12]. In our preliminary studies, the Ti-15Zr-15Mo alloys showed good quality for use as implantable materials, because they presented better combination of microhardness and Young's modulus than Ti-6Al-4V and CP-Ti[13-15], tribocorrosion resistance superior than CP-Ti[16], and cytotoxicity similar to CP-Ti-cp[15,17].

Bacterial infection of metallic implants has been indicated as one of the main factors for failure, once the material is kept in contact with the bone tissues[18]. In general, studies in the United States show that up to 10% of revision surgeries in hip prostheses are caused by infections[19]. Antibacterial action elements have been an alternative to the use of some metallic implants for the long-term[18,20]. Silver (Ag) is an antibacterial element that can inhibit bacterial growth through its enzymatic activity[6]. As an alloying element, the metal can improve the mechanical and corrosion strength and decrease Young's modulus of Ti-based materials[20]. Even its biocompatibility is restricted to low amounts of the element. The antibacterial action of Ag can be detected with the addition of only 1 wt% in a solid solution. Several studies have been developed in this area to produce and characterize, by different techniques, metallic alloys with antibacterial action by adding Ag in their composition, as Lei et al.[21], Jiang et al.[22] and Szaraniec and Goryczka[23].

With the aims to improve the mechanical properties and to insert an antibacterial action in the Ti-15Zr-15Mo alloy, this study focused on the effect of Ag addition (1 and 3 wt%) in the crystalline structure, microstructure and selected mechanical properties on this alloy, targeting biofunctional implantable material applications.

EXPERIMENTAL

The materials were obtained from commercially pure metals in an argon arc-melting furnace, with a water-cooled copper crucible and non-consumable tungsten electrode. Homogenization heat-treatment was conducted at a vacuum of 10^{-5} Pa, a heating rate of 10 K/min, a plateau of 1,273 K, during 43.2 ks, and a cooling rate of 5 K/min. After that, a hot-rolling treatment was performed at 1,273 K with air cooling. Finally, a solution treatment was done to stress relief, with a vacuum of 10^{-5} Pa, a heating rate of 10 K/min, a plateau of 1,123 K, for 21.6 ks, and water quenching.

Chemical analysis was carried out by density measurements through Archimedes' principle, inductively coupled plasma optical emission spectrometry (ICP OES; Varian spectrometer), and infrared absorption (LECO TC-400). A semi-quantitative micro-chemical analysis was performed by X-ray energy dispersion spectrometry (EDS; Oxford detector, INCA X-Act) with chemical mapping, and quantification of the alloying elements (Ti, Zr, Mo and Ag) was collected in three distinct regions during 60 s.

Structural analysis was conducted by X-ray diffraction measurements (XRD; Rigaku diffractometer, MiniFlex 600), with monochromatic Cu-K_α radiation (λ = 0.154 nm), at 40 kV and 20 mA. Cell parameters were obtained through Bragg's law applied to the diffraction peaks. Microstructural analysis was performed by optical (Olympus BX51M microscope) and scanning electron microscopy (SEM; EVO LS15, Carl Zeiss Inc.). Finally, selected mechanical properties were evaluated by Vickers microhardness and Young's modulus measurements. Vickers microhardness was acquired (Mitutoyo MicroWizard durometer), with a load of 0.300 kgf (2.942 N) for 15 s, following standard procedures[24]. Young's modulus values were obtained from the impulse excitation technique (Sonelastic equipment, ATCP Physical Engineering Corp.), following standard procedures[25].

RESULTS AND DISCUSSION

For this study, it was produced two ingots of 80 g (Ti-15Zr-15Mo-1Ag and Ti-15Zr-15Mo-3Ag). The ingots' chemical analysis showed a composition close to the nominal values, a low content of impurities and low levels of oxygen and nitrogen gas, within the standard specification for CP-Ti (grade 2), indicating the good chemical quality of the samples. Chemical mapping of the samples exhibited good distribution of the alloying elements, indicating good homogeneity without segregating precipitation. The density values were 5.23 and 5.28 g/cm3 to the Ti-15Zr-15Mo-1Ag and Ti-15Zr-15Mo-3Ag samples, respectively, values close to the theoretical ones, having the increase occurred as a result of the higher density of Zr (6.52 g/cm^3), Mo (10.2 g/cm^3) and Ag (10.5 g/cm^3), in comparison to Ti (4.51 g/cm^3)[26].

Figure 1 presents the XRD patterns of the samples on each processing condition. All peaks came from the β phase of Ti. The thermomechanical treatments did not produce phase transformation, as it did not observe any peaks from other phases. The alloying elements, Zr and Mo, acted as β-stabilizers in accordance with Correa[9]. From XRD, the cell parameter values of the β phase were obtained: 0.3297 ± 0.0007 nm to the Ti-15Zr-15Mo-1Ag sample and 0.3296 ± 0.0002 nm to the Ti-15Zr-15Mo-3Ag sample. They remained lower than CP-Ti (0.3320 nm) and closer to the Ti-15Zr-15Mo alloy (0.3290 nm). This result occurred due to the atomic radii of Ag (0.172 nm), which is greater than Ti (0.147 nm) and Mo (0.137 nm) and comparable to the Zr (0.230 nm)[26].

Figure 2 presents the micrographs of the microstructure of the samples on each thermomechanical treatment. The microstructural analysis followed the XRD results, showing only equiaxial grains of β phase. It can be observed that the as-casted samples exhibited irregular β phase grains due to the non-homogeneous cooling inside the casting chamber, in which part of the sample was cooled in argon and the bottom part by the water-cooled copper crucible. The homogenization heat treatment produced an increase of the grain to values higher than 500 μm and angles between boundaries of around 120°. The thermomechanical processing in the hot-rolled condition resulted in many dislocations in the microstructure, forming irregular grains with an average size lesser than 100 μm. After solution treatment, there was only an increase in the average grain size due to eliminate the dislocations. In a general view, apparent differences in the microstructure in each sample were not observed.

Figure 3 presents the Vickers microhardness values of the samples compared with CP-Ti and Ti-15Zr-15Mo alloy. It is possible to see that the Ag concentration did not significantly change the studied material's microhardness. However, the homogenization and hot-rolling treatments promoted decrease in the microhardness values as a result of the grain growth and preferential orientation, respectively. The microhardness values of the samples and Ti-15Zr-15Mo were higher than CP-Ti. Besides the solid solution strengthening of the Zr and Mo atoms in the sample, the Ag promoted a slight softening effect, decreasing the material's hardness.

Figure 4 shows Young's modulus values of the samples compared with CP-Ti and Ti-15Zr-15Mo alloy. According to the graph, the thermomechanical processing did not modify this property in the samples. Furthermore, the chemical composition had no significant influence on the average values, remaining within the values' standard deviation. The Ag content promoted a little increase in Young's modulus values, possibly because of the bound energy changes between the atoms with the metal. Even so, Young's modulus values of the samples remained below the commercial material CP-Ti and highlight that the materials remain with great potential to avoid the stress shielding effect.

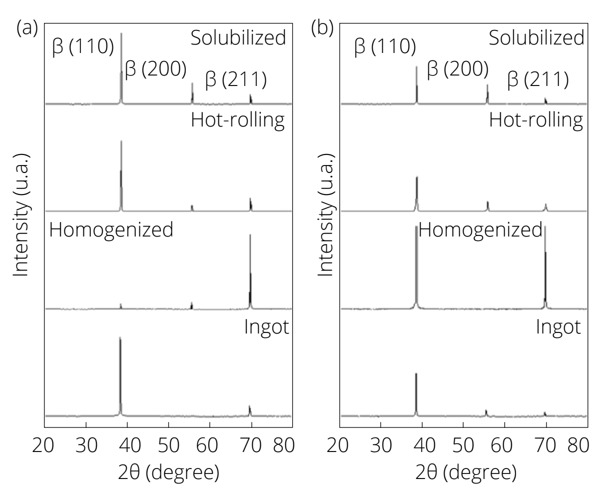

Figure 1: X-ray diffraction patterns for samples of (a) Ti-15Zr-15Mo-1Ag and (b) Ti-15Zr-15Mo-3Ag.

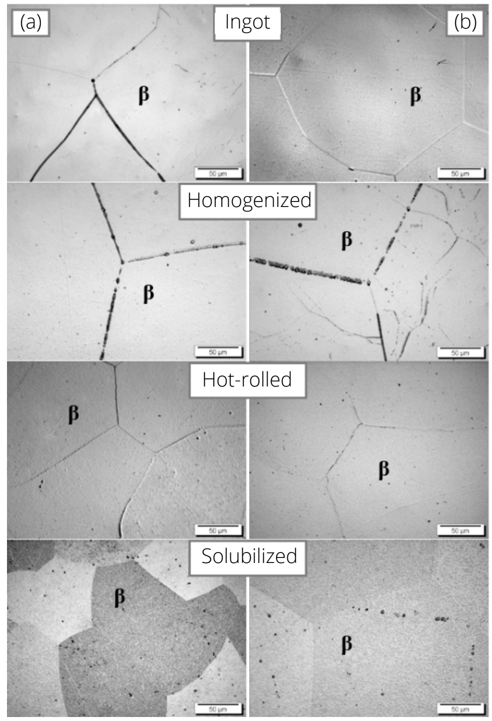

Figure 2: Micrographs of the samples of (a) Ti-15Zr-15Mo-1Ag and (b) Ti-15Zr-15Mo-3Ag alloys.

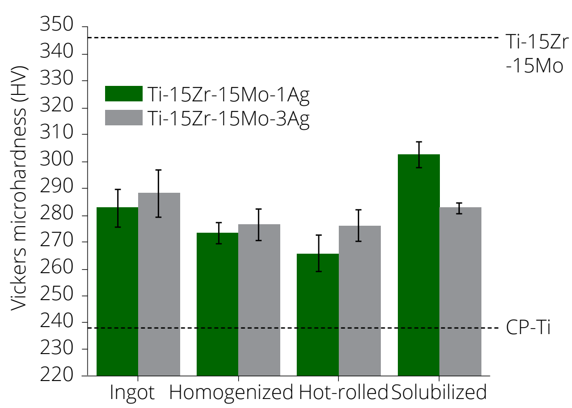

Figure 3: Vickers microhardness of the alloys.

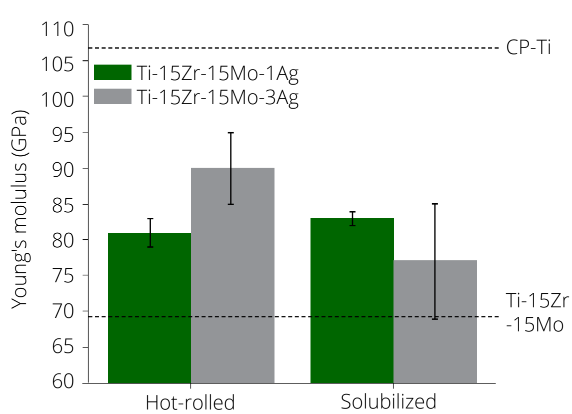

Figure 4: Young's modulus of the alloys.

CONCLUSION

The obtained samples Ti-15Zr-15Mo-1Ag and Ti-15Zr-15Mo-3Ag possessed only peaks from the β phase of Ti, and the low Ag content did not significantly affect the selected mechanical properties, remaining with values better than CP-Ti. According to the results presented, the samples have great potential for applications as a biomaterial, and the Ti-15Zr-15Mo-1Ag could be the best choice to be used as a biofunctional implantable material.

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DATA AVAILABILITY STATEMENT

Data can be shared upon request.

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