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Dynamical Elastic Moduli of the Ti-13Nb-13Zr Biomaterial Alloy by Mechanical Spectroscopy

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Dynamical Elastic Moduli of the Ti-13Nb-13Zr biomaterial alloy were obtained using the mechanical spectroscopy technique. The sample with heat treatment at 1170K for 30 minutes and water quenched with subsequent aging treatment at 670 K for 3 hours (TNZ + WQ + 670 K/3 h), was characterized through decay of free oscillations of the sample in the flexural vibration mode. The spectra of anelastic relaxation (internal friction and frequency) in the temperature range from 300 K to 625 K not revealed the presence of relaxation process. As shown in the literature, the hcp structure usually does not exhibit any relaxation due to the symmetry of the sites in the crystalline lattice, but if there is some relaxation, this only occurs in special cases such as low concentration of zirconium or saturation of the stoichiometric ratio of oxygen for zirconium. Dynamical elastic modulus obtained for TNZ + WQ + 670 K/3 h alloy was 87 GPa at room temperature, which is higher than the value for Ti-13Nb-13Zr alloy (64 GPa) of the literature. This increment may be related to the change of the proportion of α and β phases. Besides that, the presence of precipitates in the alloy after aging treatment hardens the material and reduces its ductility.

Keywords: *Ti-13Nb-13Zr, aging treatment, elastic modulus, anelastic relaxation*

1. Introduction

Titanium and titanium alloys have a great clinical interest as biomaterials for use as materials for artificial implants (orthopedic or dental) for its high biocompatibility, excellent corrosion resistance and appropriate mechanical properties compared to stainless steels and alloys of Co-Cr. This alloys are distinguished by its low modulus of elasticity, closed to that of human bone (10-40 GPa), which ensure the adequate mechanical stress transfer to the surrounding bone[1].

Nowadays the Ti-6Al-4V alloy is the major biomedical alloy used on orthopedic implants, but has a disadvantage because of its high modulus of elasticity (110 GPa), in addition that, recent studies revealed that the presence of Al and V ions are harmful to health in the long term implants[2-4]. Thus, among the new research of alloys for biomedical applications based in titanium free of toxic elements and with appropriate mechanical properties and high biocompatibility the Ti-13Nb-13Zr (TNZ) alloy appears as an option to be taken into account because the processing variables can be controlled to lead selected results[4].

Ti-13Nb-13Zr alloy is typically an near-β Ti alloy which, when heat treated up the β-transus temperature and water-quenched posses a hexagonal α´-phase martensite microstructure, but followed by an aging treatment that is transformed into a martensite formed by α-phase (hcp structure) with precipitates of β–phase (bcc structure)[5-7].

In general it is of great interest to know in a metallic alloy the behavior of alloying elements and the mechanical properties, specifically the elastic modulus in biomaterials, therefore the mechanical spectroscopy becomes an important tool for characterization because it can provide information about the interaction of the matrix with the solutes atoms (substitutional and interstitial)[8-11], besides dynamical elastic modulus (elastic modulus as function of temperature)[12] parameter of great importance from the viewpoint of biocompatibility.

This paper presents results of anelastic relaxation and elastic modulus as function of the temperature, obtained by mechanical spectroscopy from the flexural vibration of the fundamental mode of Ti-13Nb-13Zr alloy samples submitted to heat treatment of 1170 K for 30 minutes and water quenched with subsequent aging treatment to 670 K for 3 hours.

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2. Experimental Part

Starting from commercially pure materials Ti, Nb, Zr, were obtained ingots of 18 mm diameter Ti-13Nb-13Zr alloy by arc melting in an atmosphere of argon. Then the ingots were subjected to cold swaging yielding rods of 6 mm diameter corresponding to 89% of plastic deformation. So, after of annealed at 1170 K for 30 minutes and water quenched, an aging treatment for 3 hours at a temperature of 670 K was performed in this sample, the sample was labeled as TNZ + WQ + 670 K/3 h. Crystalline phases and microstructure of the sample were characterized by X-ray diffraction (XRD) and scanning electron microscopy (SEM).

The ingots were cut into rectangular bar shape and additionally was performed successive etching in an acid solution of 2 mL HF + 10 mL HNO 3 + 8 mL H2O until get a bar with dimensions of $4.62 \times 20.66 \times 0.54$ mm^3 and free from impurities on the surface conditions appropriate for measurements of mechanical spectroscopy.

Anelastic relaxation spectra (Internal friction and frequency as function of the temperature) were obtained by the Acoustic Elastomer System (Vibran Technology®, Model AE-102)[13] in the temperature range of 300 K to 625 K with a heating rate of 1 K/min and pressure of about 10^{-5} Torr.

Mechanical spectroscopy is a characterization technique which measures the absorbed energy (internal friction (Q^{-1})) by the solid when it is subjected to a mechanical oscillating stress with a certain frequency (ω)[14]. The internal friction is related to the anelastic strain suffered by the solid since the atomic rearrangement processes require a relaxation time to obtain a new state of equilibrium.

Since the stress and strain have a temporal dependence for real solid, from Hooke's Law the dynamical elastic modulus (E) to an oscillating mechanics wave, can be written[12,14,15]:

$$E(\omega) = \frac{\sigma^*}{\varepsilon^*} = E' + iE'' \tag{1}$$

where E' and E'' represent the storage and loss dynamical elastic modulus. Thus from the tangent angle of lag (ϕ), corresponding to the difference between the imaginary and real parts of the dynamical elastic modulus, is possible determine the energy absorbed by the solid, or internal friction (Q^{-1}), besides, to flexural vibrations the internal friction (Q^{-1}) can be obtained from the logarithmic decrement (γ) of the free oscillations of the sample

$$Q^{-1}(\omega,T) = \frac{E''}{E'} = \tan(\varphi) = \frac{\gamma}{\pi} \tag{2}$$

where logarithmic decrement (γ).

In clamped free geometry, such as Acoustic Elastomer System the relation between resonant frequency of fundamental tone (f_1) and dynamical elastic modulus (E), can be written[12]:

$$f_1 = 0.1615\frac{h}{l^2}\sqrt{\frac{E}{\rho}} \tag{3}$$

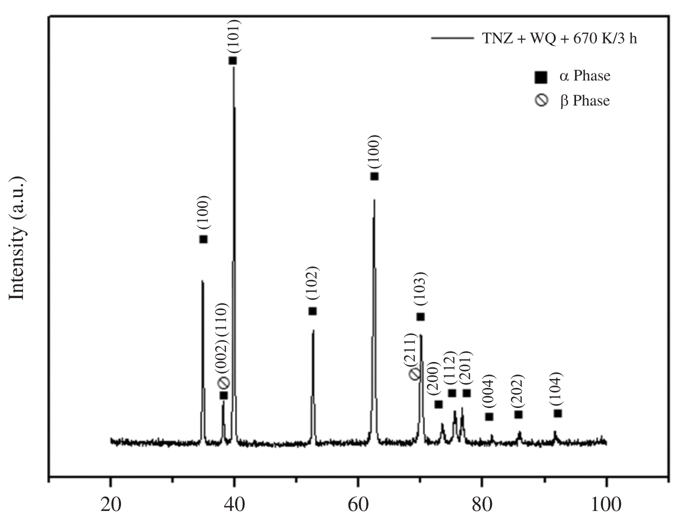
where h is thickness l is the length and ρ is the density of the sample.

3. Results and Discussion

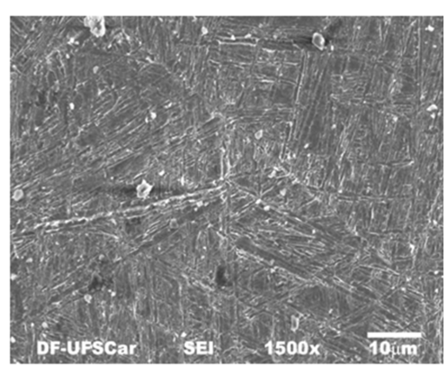
Figure 1a shows the X ray diffraction pattern of the sample TNZ + WQ + 670 K/3 h, where can be observed the presence of α and β phases with structure hcp and bcc respectively, which are in agreement with the observed in the literature[2,5,7] for this titanium alloy when submitted to aging treatment.

In the Figure 1b, the micrograph obtained by SEM revealed the presence of a matrix of α-phase with a dispersion of β-phase precipitated, which is in agreement with XRD results.

Figure 2 shows the anelastic relaxation spectra, internal friction and oscillation frequency, as function of temperature for TNZ + WQ + 670 K/3 h sample, where for the temperature range studied were not observed relaxation processes.



(a)



(b)

Figure 1. (a) DRX patterns and (b) SEM micrographs for TNZ + WQ + 670 K/3 h sample.

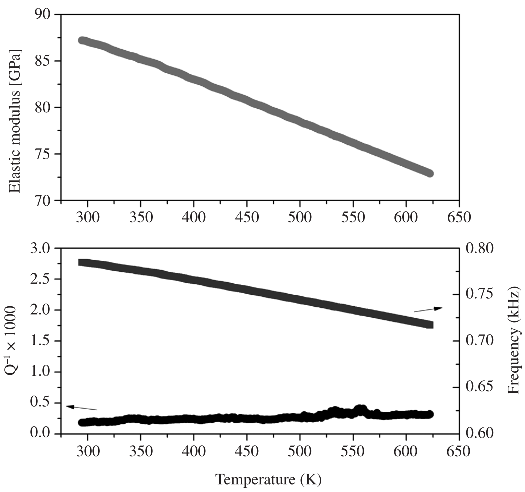


Figure 2. Anelastic relaxation spectra and dynamical elastic modulus for TNZ + WQ + 670 K/3 h alloy.

The absence of relaxation processes can be associated in first instance, with the hcp structure presented by this alloy, since the interstitial sites, octahedral and tetrahedral, have tetragonal symmetry equal to those atoms in the lattice, so simple interstitial atoms do not produce anelastic relaxation[11,16,17]. Moreover in titanium alloys, like Ti-O-Me (Me being a metal such as Zr or Nb), relaxation processes were found only from the individual atoms of oxygen trapped in the vicinity of substitutional atoms by the distortion that these last produce in the lattice. But in this case as the atomic radius of Nb and Ti are close the contribution to distortion of Nb element can be neglected. Concerning to Zr, this contributes to the distortion of octahedral sites, but the increase of its contribution decreases the solubility of O, so studies will revealed that only one relaxation peak is observed to a maximum concentration of 0.06% at. Zr, then the peak intensity decreases[18]. Besides, it was observed by other researchers in alloys containing Zr as substitutional element and O as interstitial atom, that the presence of substitutional elements affect the random distribution of the interstitial solute atoms in free solid solution and the anelastic relaxation process is observed only after the saturation of the stoichiometric ratio of O to Zr[9,19,20].

The dynamical elastic modulus for TNZ + WQ + 670 K/3 h sample was determined from flexural resonance frequency of fundamental tone of bar in clamped-free geometry using the Equation 3. The value of density of the alloy used in the equation was 4,767 ± 0.006 $g.m^{-3}$ obtained by the Arquimedes experimental method. Was observed a decrease in elastic modulus value for high temperature, as is typical in this kind of alloys. The value of dynamical elastic modulus at room temperature of TNZ + WQ + 670 K/3 h alloys obtained by flexural vibrations is 87 GPa. The difference between the values of dynamical elastic modulus observed in this work for Ti-13Nb-13Zr with aging treatment and literature data for Ti-13Nb-13Zr without aging treatment (61.9 GPa)[21], can be associated with the change of the proportion of α and β phases which contributes atypically for elastic modulus value of the material, besides that, the presence precipitates in the alloy after aging treatment harden the material and reduce its ductility[22,23].

4. Conclusions

Ti-13Nb-13Zr alloy subjected to heat treatment of the aging 670 K/3 h, shows no anelastic relaxation process due to interstitial or substitutional solutes. As was mentioned above, the hcp structure difficultly relaxes due to the symmetry of the sites in the lattice, besides, the relaxation that occurs will be only for special cases: low concentration of Zr (<0.06% at.) and saturation of the stoichiometric ratio of O for Zr. Moreover, the module of elasticity is sensitive to aging treatment compared with data of the literature for this same alloy without aging treatment.

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