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Anelastic relaxation due to hydrogen in Ti–35Nb–7Zr–5Ta alloy

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ABSTRACT

Titanium and its alloys are frequently used in the production of prostheses and dental implants due to their properties, such as high corrosion resistance, low elasticity modulus, and high mechanical strength/density relation. Among the Ti-based alloys, Ti–35Nb–7Zr–5Ta (TNZT) is one that presents the smallest elasticity modulus (around 45 GPa), making it an excellent alternative to be used as a biomaterial. In this paper, mechanical spectroscopy measurements were made of TNZT alloys containing several quantities of hydrogen in solid solution. Mechanical spectroscopy measurements were made by using a torsion pendulum, operating at an oscillation frequency in the interval 2–20 Hz, temperature in the range 100–300 K, heating rate of about 1 K/min, and vacuum lower than 10^{-5} Torr. A relaxation structure and a reduction in the elasticity modulus were observed for the heat-treated and doped samples. The observed peak was associated with the interaction of hydrogen trapped by oxygen atoms around the titanium atom of the metallic matrix.

1. Introduction

The study of the behavior of group V metals with interstitial impurities such as oxygen, nitrogen, carbon, and hydrogen in solid solution has been piquing several researchers' interest, because such impurities can modify the mechanical properties of these metals [1].

The interaction among substitutional solute atoms in metals has given origin to several experimental studies, because such information is fundamental for the understanding of many basic physical processes, such as short-range ordering, segregation, and diffusion, among others. The interaction energies are necessary for calculations of phase diagrams and the mechanical and physical properties of solid solutions [2].

The interstitial atoms in solid solution dissolved in metals with body-centered cubic (bcc) structure cause a deviation in the perfect elasticity known with anelasticity. Snoek's experimental work performed on samples of iron with carbon in solid solution made it possible to establish the theoretical basis for the observed effects. This effect is known as the Snoek effect. In the Snoek effect, a stress-induced ordering occurs through the jump of interstitial atoms into equivalent sites around the atoms of the metallic matrix [3,4]. A very sensitive technique to study atomic movement is mechanical spectroscopy, a non-destructive test that supplies information regarding the presence and behavior of these interstitial elements [5,6].

In the absence of stress, the interstitial atoms are randomly distributed at the sites with tetragonal or octahedral symmetry. When a mechanical stress is applied, a redistribution of the interstitial atoms for energetically equivalent sites occurs. Each specimen of interstitial solutes gives origin to a peak in the anelastic spectrum, which can be observed at different temperatures (depending on the frequency) [7,8].

Hydrogen interstitials atoms have also been shown to be strongly trapped by other point defects and by dislocations, with a resultant decrease in long-range diffusivity. In particular, evidence has been presented for the formation of O–H pairs in niobium, for which the binding enthalpy is sufficiently large so as to prevent NbH precipitation, when the oxygen concentration exceeds the hydrogen concentration [9].

Internal friction peaks caused by the stress-induced ordering of O–H pairs in niobium have been measured over a wide temperature range. The ordering, in which the hydrogen interstitial jumps around an essentially immobile oxygen interstitial trapping site, is characterized by an Arrhenius temperature dependence at temperatures above 100 K [10].

The trapping of hydrogen by substitutional impurities was first reported for Nb–Ti–H dilute alloys [11]. It was found by Gorsky effect measurements that the hydrogen diffusion coefficient progressively and noticeably decreases with increasing titanium concentration, and concomitantly the activation energy for diffusion increases. The anelastic measurements indicated that

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Table 1
Chemical analysis of the TNZT#1 sample.

Element	Ti	Nb	Zr	Ta
Content (wt%)	(52.3 ± 0.4)	(35.2 ± 0.4)	(7.5 ± 0.4)	(5.0 ± 0.2)

substitutional titanium is a very effective trapping center for hydrogen, which is able to remove this element from solid solution and to retain it in its neighborhoods, thus inhibiting hydride precipitation [12]. The presence of interaction peaks and their shifts with the hydrogen content were also found a few years later in V–Ti dilute alloys [13]. Cannelli et al. [14] investigated the symmetry of the substitutional–interstitial complex in single crystals and found that substitutional Ti atoms in Nb can act as such trapping centers. Similar trapping effects were also found in face-centered cubic (fcc) metals [15].

Grandini et al. [16] investigated the Nb–Zr–O–H system by ultrasonic measurements and found a thermally activated relaxation structure at 202 K and 235 K (for 10 MHz and 30 MHz, respectively) where the intensity increased with the increase in hydrogen content and was attributed to the stress-induced ordering of hydrogen atoms around oxygen atoms present in the sample.

Recently, Mugishima et al. [17] studied the Ta–O–H system, and the hydrogen diffusion was measured in order to investigate the interaction between oxygen and hydrogen in tantalum. They observed that the diffusivity of hydrogen is reduced with the oxygen concentration by the trapping effect of interstitials and substitutionals.

Then, the presence of substitutional solute strongly changes the anelastic spectrum, especially when there is interaction with interstitial atoms.

This paper presents a study on the influence of the concentration of hydrogen in the anelastic properties of Ti–35Nb–7Zr–5Ta (TNZT) alloys, using low temperature mechanical spectroscopy measurements.

2. Experimental

The samples used in this paper constitute polycrystals of the Ti–35Nb–7Zr–5Ta alloys, produced by arc-melting with a water-cooled crucible, in the Materials Engineering Department of the Universidade de Campinas (Campinas, Brazil). Titanium, niobium, zirconium, and tantalum with a purity of 99.99% (Sigma–Aldrich, Inc.) were used. After melting, the samples were submitted to a swaging, to obtain cylindrical samples with a diameter of approximately 3.0 mm. Under these conditions, the sample was labeled TNZT#1. Table 1 shows the chemical analysis of the prepared samples, measured using Vista plasma atomic emission spectroscopy (Varian, Inc.).

In addition to the as-received condition (TNZT#1), the samples were measured after annealing in ultra-high vacuum (5×10^{-9} Torr) at 1273 K for 2, 4 and 6 h (TNZT#2, TNZT#2a, and TNZT#2b, respectively), followed by two heat treatments in hydrogen atmosphere at 773 K with partial pressures of 1 atm (TNZT#22) and 0.5 atm (TNZT#23) of hydrogen for 30 min, and fast cooling to room temperature. The hydrogen charges were conducted at the Physics Institute of the Universidad de la Republica (Montevideo, Uruguay). The interstitial contents are presented in Table 2, and were obtained using a TC-136 (Leco Co.) apparatus (for oxygen and nitrogen), and an RH2 (Leco Co.) apparatus (for hydrogen).

The measured anelastic spectra were obtained using the torsion pendulum technique, whose operation principle is very simple, where the sample is put to oscillate in its fundamental mode, in free oscillations, which causes energy dissipation due to the internal friction. This energy dissipation is directly related to the logarithmic decrement of the oscillation amplitude. The method used to measure the logarithmic decrement was the velocity method, which relates the logarithmic decrement to the oscillation time. The measurements were performed with a frequency in the interval 2–20 Hz in a temperature range of 100–700 K (but in this paper we analyzed the 100–300 K range), and in a vacuum better than 10^{-5} Torr at a heating rate of approximately 1 K/min. The data were obtained by an automatic system, which measured the angular velocity of the pendulum around the equilibrium position [18].

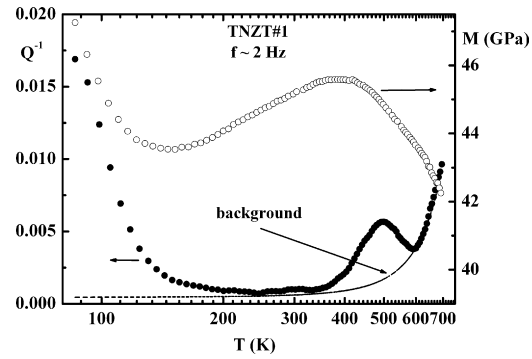

Fig. 1. Anelastic spectrum for the TNZT#1 sample, measured with a frequency of approximately 2 Hz [19].

3. Results and discussion

Fig. 1 presents the anelastic spectrum (internal friction, Q^{-1}, and elasticity modulus, M) obtained for sample TNZT#1 [19]. It is possible to identify the presence of two relaxation structures (peaks), which can be associated with the interaction of hydrogen atoms (low temperature peak) and oxygen (or nitrogen) atoms (high temperature peak) with the atoms of the alloy. Another characteristic behavior of a relaxation process is the step in the curve of the elasticity modulus that is related to the oscillation frequency of the system [3].

In another paper [19], the high temperature peak was analyzed. This relaxation structure is thermally activated, influenced by the concentration of interstitial elements (mainly oxygen), asymmetric, and broad, indicating that this relaxation structure is composed of several relaxation processes. The complex relaxation structures were resolved into six elementary Debye peaks, corresponding to stress-induced ordering of oxygen atoms sitting in octahedral sites around the four elements that compose the alloy (Ti–O, Nb–O, Zr–O, and Ta–O relaxation processes) and of pairs of oxygen atoms around the titanium and niobium atoms, elements found in major quantities in the alloy (Ti–O–O and Nb–O–O relaxation processes).

In order to verify the behavior of the low temperature anelastic relaxation structure in Fig. 1, the internal friction was measured at four different frequencies: 2, 4, 12, and 17 Hz. Fig. 2 presents a comparison among the anelastic spectra measured with different frequencies after background extraction. Several mechanisms can be responsible for the internal friction background in the absence of phase transformations. In our case, a possible explanation for the background is the magneto mechanical damping accompanied by hydrogen reorientation around solute atoms. It is possible to observe that the relaxation structure moves to higher temperatures with increases in the oscillating frequency (in spite of the experimental limitations), denoting the thermally activated behavior of the relaxation structure. This is another characteristic of a peak that represents a relaxation process due to stress-induced ordering of point defects [20]. The internal friction background was estimated by interpolation between the measured internal friction levels on both sides of the maximum at a sufficiently large distance from it. An exponential growth function was used for background interpolation, as can be seen in Fig. 1.

Table 2
Oxygen nitrogen and hydrogen concentration in the TNZT samples.

Element	Sample					
	TNZT#1 (wt%)	TNZT#2 (wt%)	TNZT#2a (wt%)	TNZT#2b (wt%)	TNZT#23 (wt%)	TNZT#22 (wt%)
O	0.271 ± 0.006	0.232 ± 0.004	0.253 ± 0.006	0.28 ± 0.03	0.275 ± 0.003	0.24 ± 0.04
N	0.06 ± 0.06	0.058 ± 0.002	0.042 ± 0.001	0.037 ± 0.003	0.044 ± 0.004	0.042 ± 0.003
H	0.028 ± 0.004	0.013 ± 0.004	0.010 ± 0.002	0.008 ± 0.002	0.078 ± 0.004	0.188 ± 0.005

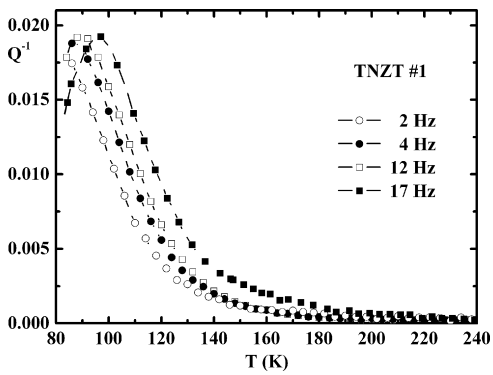

Fig. 2. Anelastic spectra without background for the sample TNZT#1 measured on heating at different frequencies.

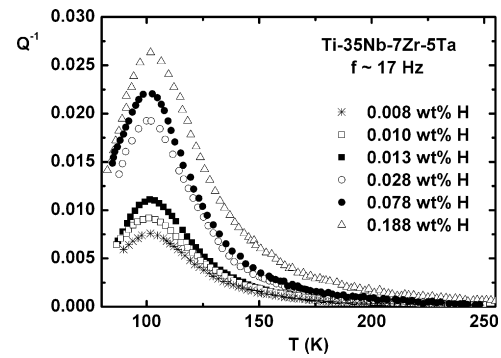

Fig. 4. Anelastic spectra without background for the TNZT samples measured on heating at 17 Hz, for several quantities of hydrogen.

The diffusion of hydrogen occurs with low energy, then, during the successive heat treatments (or measurements on heating until 700 K); it can hasten the migration of hydrogen to the surface. As the heat treatments (or measurements) were made in ultra-high (or high) vacuum, a reduction of hydrogen can occur in the samples.

Fig. 3 shows a comparison among the spectra measured before and after heating up to 700 K in high vacuum. A reduction in the intensity of the peak can be observed, indicating that a portion of some interstitial element was lost with the heating in vacuum. To verify the nature of the interstitial element, the samples were submitted to several heat treatments in vacuum or in hydrogen atmosphere. Fig. 4 presents a comparison among the anelastic spectra for TNZT samples, measured at a frequency of approximately 17 Hz, with different quantities of hydrogen. It can be observed that the intensity of the relaxation structure increases with increasing hydrogen content, showing that the relaxation structure is clearly related with hydrogen.

A large number of mechanical spectroscopy investigations have been made with several bcc pure metals and alloys in order to clarify the nature of the complex interaction among the interstitial solutes and the alloy components [20]. The interstitial elements interact with the substitutional and metallic matrix elements by a relaxation process known as stress-induced ordering. This relaxation process is represented by a Debye peak [3,21]:

$$Q^{-1} = \frac{Q_m^{-1}\,T_m}{T}\,\mathrm{sech}\left(\frac{H}{k}\left(\frac{1}{T_m} - \frac{1}{T}\right)\right) + \ln\left(\frac{f(T)}{f_m}\right) \quad (1)$$

where: Q_m^{-1} is the intensity, T_m is the peak temperature, T is the absolute temperature, f_m is the frequency, and H is the activation enthalpy of the relaxation process associated with the peak; f is the frequency, k is the Boltzmann constant, and T is the absolute temperature.

The internal friction spectra were analyzed by using the peak-fitting modulus of the Microcal Origin® software, and Fig. 5 shows the results for two samples, the one as-received and the other with a higher quantity of hydrogen. It is interesting to observe that the relaxation peak is symmetric. This is a characteristic of relaxation structures composed by a single relaxation process [3,20]. The activation enthalpy obtained for this relaxation process was (0.16 ± 0.03) eV.

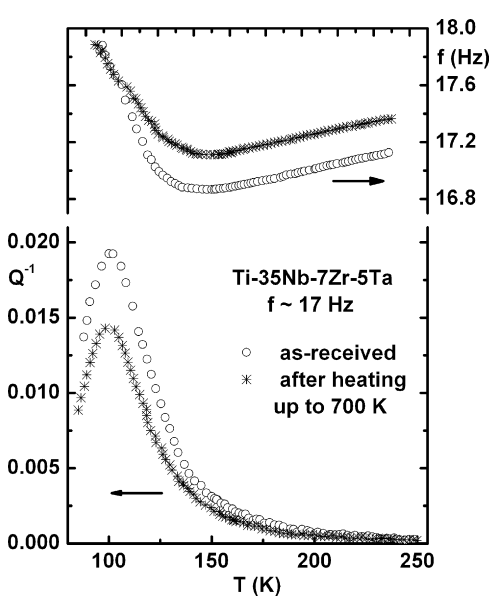

Fig. 3. Anelastic spectra for the sample TNZT#1 measured on heating after and before a heating up to 700 K.

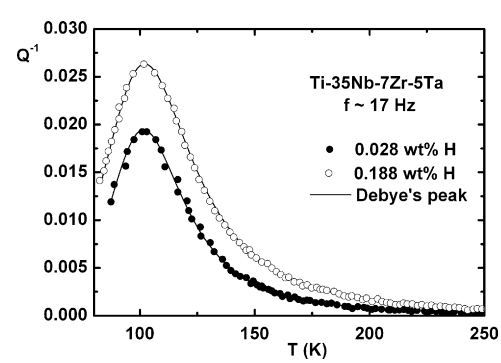

Fig. 5. Analysis of two anelastic spectra without background for the TNZT samples measured on heating at 17 Hz.

There were several studies of internal friction in the bcc elements (as for example Nb, Ta, Zr, and Ti). Wipf et al. [22] studied polycrystalline samples of Ti and Zr containing hydrogen using mechanical spectroscopy data measured with the vibrating reed technique. In these metals, the hydrogen atoms occupy tetrahedral interstitials, forming a simple cubic lattice in the fcc δ-phase. The jump rates follow an Arrhenius relation with activation enthalpies of 0.496 eV for the diffusion of hydrogen atoms in the titanium and zirconium metallic matrix. Yoshinari and Koiwa [23,24] studied polycrystalline samples of Nb and Ta containing hydrogen using the torsion pendulum technique, and obtained 0.114 eV and 0.084 eV for the activation enthalpies of the diffusion of hydrogen atoms by jumps into interstitial tetrahedral equivalent sites in the niobium and tantalum metallic matrix, respectively.The presence of substitutional atoms in Nb based alloys containing hydrogen and oxygen (or nitrogen) in solid solution increases the value of the activation enthalpy [13,25,26]. In all of the studies, the heavy interstitial atoms acted as traps for hydrogen atoms. The interstitial solutes are located in octahedral sites near the substitutional solute atoms, and the activation energy for their reorientation jump was found to increase, so that the corresponding peak shifts towards a higher temperature [27].

By comparing our results with the literature, it is clear that the observed peak is due to the stress induced ordering of hydrogen atoms around essentially immobile oxygen interstitial atoms in the lattice of the Ti–Nb–Zr–Ta alloy, the called O–H pair.

4. Conclusion

Mechanical spectroscopy measurements were made in TNZT alloys used as biomaterial and the presence of two relaxation structures was observed, one in the low temperature region and another in the high temperature region. These relaxation structures are thermally activated and are influenced by the concentration of interstitial elements (mainly oxygen).

The relaxation structure at low temperature is strongly dependent on hydrogen and was attributed to the stress induced ordering of hydrogen atoms around oxygen interstitial trapping atoms in the Ti–35Nb–7Zr–5Ta alloy, with activation enthalpy of 0.16 eV for the jumps into equivalent tetrahedral sites.

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