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Effect of heavy interstitials on anelastic properties of Nb-1.0 wt% Zr alloys

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Abstract The mechanical properties of metals with bcc structure, such as niobium and its alloys, have changed significantly with the introduction of heavy interstitial elements. These interstitial elements (nitrogen, for example), present in the alloy, occupy octahedral sites and constitute an elastic dipole of tetragonal symmetry and might produce anelastic relaxation. This article presents the effect of nitrogen on the anelastic properties of Nb-1.0 wt% Zr alloys, measured by means of mechanical spectroscopy using a torsion pendulum. The results showed complex anelastic relaxation structures, which were resolved into their constituent peaks, representing each relaxation process. These processes are due to stress-induced ordering of the interstitial elements around the niobium and zirconium of the alloy.

Introduction

The interest in technological development led to the discovery of several niobium alloys to be used mainly in the aerospace and nuclear industries. Among these alloys, Nb-1.0 wt% Zr (Nb1Zr) is highlighted, because it presents good rigidity, high hardness, great thermal stability, and an excellent corrosion resistance.

Metals and alloys with solutes dissolved interstitially in solid solution present anelastic behavior due to a process known as stress-induced ordering [1]. Internal friction is a manifestation of anelasticity, which was initially observed by Snoek [2] in α-iron with carbon and nitrogen as interstitial solutes. It is expected that, in the bcc crystalline structure of the Nb1Zr alloy, the oxygen and nitrogen atoms occupy similar positions to carbon and nitrogen in the α-iron crystalline structure [2]. The interstitial sites that oxygen and nitrogen occupy in this Nb–Zr alloy are of the octahedral type, giving rise to a strain tensor of tetragonal symmetry [1]. In these alloys, interstitial atoms interact elastically and chemically with the substitutional atoms and form a substitutional-interstitial complex, which reduces the Snoek peaks and introduces subsidiary peaks [3].

Mechanical spectroscopy has been used so that information about solute behavior in metals could be obtained, for example: interactions, such as solutes-metallic matrix [2], substitutional-interstitial [1, 4, 5], interstitial diffusion [6, 7], etc.

Mechanical spectroscopy measurements in the Nb–Zr alloys have shown that the addition of zirconium reduces and enlarges or completely removes the relaxation peaks [3, 8–11]. In contrast to non-alloyed niobium, the presence of substitutional zirconium introduces new peaks due to the substitutional-interstitial interactions. Earlier studies performed in Nb–Zr with only oxygen in solid solution using mechanical spectroscopy [10] showed anelastic relaxation spectra, which were decomposed into their constituent peaks and were attributed to the stress-induced ordering of oxygen atoms, pairs of oxygen atoms and triplets of oxygen atoms around the niobium and/or zirconium that forms the alloy.

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In the present article, mechanical spectroscopy (internal friction and frequency) was measured as a function of temperature for the Nb1Zr alloy, not only with oxygen, but also with oxygen and nitrogen as interstitial solutes, with the objective of studying the effect of nitrogen on the anelastic properties of the alloy containing a fixed quantity of oxygen. The results showed complex anelastic relaxation structures, which were resolved into their constituent peaks, representing each relaxation process. These relaxation processes occur due to the stress-induced ordering of the interstitial elements around the niobium and zirconium in the alloy.

Experimental part

Polycrystals of Nb–Zr alloys, containing 1.0 wt% of zirconium were utilized as samples in the experiment and supplied by the Departamento de Engenharia de Materiais (DEMAR), at Escola de Engenharia de Lorena (USP-EEL), Lorena (SP), Brazil. The samples were produced by electron beam melting of high-purity Nb and Zr. Table 1 shows the impurities present in the Nb1Zr samples, which were detected by plasma atomic emission using Varian VISTA equipment. After the melting, the produced buttons were submitted to a swaging, in order to obtain a rod with approximately 2.7 mm in diameter. The samples were cold worked and chemically polished to a final diameter of approximately 1.0 mm. They were measured in the as-received condition, after a vacuum heat treatment and after three heat treatments in nitrogen atmosphere.

The heat treatment was performed in vacuum better than 5×10^{-8} Torr at 1,170 K for two hours, with a heating/freezing rate of 10 K/min.

The heat treatments in nitrogen atmosphere were carried out in three different conditions, always keeping the same temperature, 1,370 K, and the 10^{-4} Torr order partial pressure of nitrogen, with a variation only in time: one hour; eight hours, and ten hours. These conditions resulted in the quantities of oxygen and nitrogen presented in Table 2, obtained by using Leco TC equipment.

Table 1 Impurities present in the Nb1Zr samples

Element	Al	Si	Cu	Pb
(wt%)	0.21	<0.03	2.05	0.24

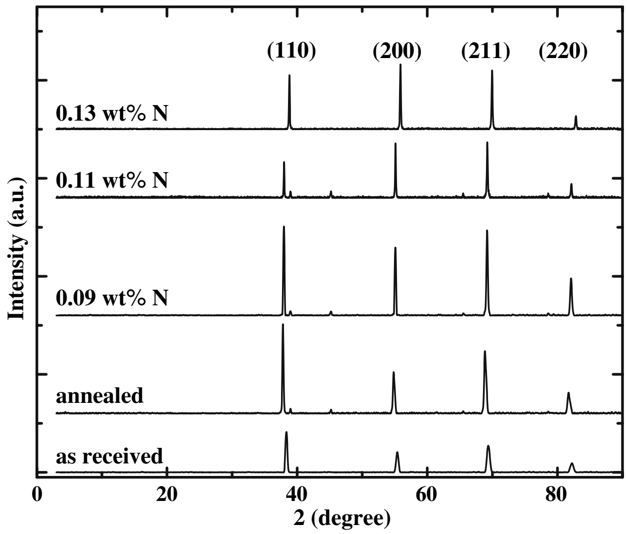

Fig. 1 X-ray diffractograms for Nb1Zr samples obtained after each nitrogen charge

After each nitrogen charge, the samples were checked by X-ray diffraction using a Rigaku D/Max 2100-PC with Cu K_α radiation, in order to verify possible structural changes due to the introduction of nitrogen. The X-ray diffractograms are shown in Fig. 1, in which one can see that there are no significant structural changes, however, there are local distortions due to the introduction of interstitial nitrogen.

The mechanical relaxation spectra were obtained in a torsion pendulum, operating at a low oscillating frequency (1.0–10.0 Hz), in a temperature range between 300–700 K, heating rate of 1.0 K/min and vacuum better than 2×10^{-6} Torr.

Mechanical spectroscopy permits measuring the elastic modulus (related to oscillation frequency) and the elastic energy loss (internal friction, Q^{-1}) as a function of temperature. In mechanical spectroscopy measurements, samples are placed for vibrating in fundamental mode (free vibrations), giving rise to energy dissipation by heating, due to internal energy absorption. Energy dissipation can be measured directly or indirectly. In the case of the torsion pendulum, this loss energy per cycle is measured by logarithmic decrement of the vibration amplitudes, which is proportional to internal friction. Internal friction can be given by the following equation [1]:

$$Q^{-1} = \frac{1}{N\pi} \ln\left(\frac{A_0}{A_N}\right) \tag{1}$$

Table 2 Oxygen and nitrogen concentration in the Nb1Zr samples

Doping	As received	Annealed	1 h	8 h	10 h
O (wt%)	0.07 ± 0.02	0.07 ± 0.02	0.4 ± 0. 2	0.4 ± 0.1	0.4 ± 0.1
N (wt%)	0.03 ± 0.01	0.03 ± 0.01	0.09 ± 0.02	0.11 ± 0.01	0.13 ± 0.01

In which N is the number of oscillations, presenting a decay in amplitude from A_0 to A_N.

The data were obtained by an automatic system, which measures the angular velocity of the pendulum around the equilibrium position [12].

Results and discussion

Figure 2 shows the mechanical relaxation spectra for the Nb1Zr sample, measured in its “as received” form and after heat treatment. The figure reveals the absence of relaxation peaks in the curve obtained before heat treatment until 550 K, in which a significant increase of internal friction towards the end of the spectrum starts. The absence of the relaxation peak can be attributed to the presence of zirconium atoms, which interact directly with the interstitial solute atoms, trapping oxygen and nitrogen atoms [3, 8, 13]. The background increase, in the high temperature zone, is characteristic of samples with a high deformation degree and with many internal stresses, which result from the cold work employed in order to maintain the sample in the appropriate dimensions to be used in the Torsion Pendulum [14]. After heat treatment, the significant increase of internal friction in the high temperature region is not observed. This can be easily explained: with heat treatment there was a relief of the residual internal stresses as a result of the alloy’s microstructural recovery [15, 16], decreasing the sample’s intrinsic internal friction. Furthermore, the presence of a complex and thermally activated relaxation structure can be observed around 500 K, which was not present before the heat treatment. After the cold work, the sample possessed small grains, which increased significantly due to heat treatment. SEM analyses (not shown here) show a significant grain growth and the absence of an oxide layer on the sample surface.

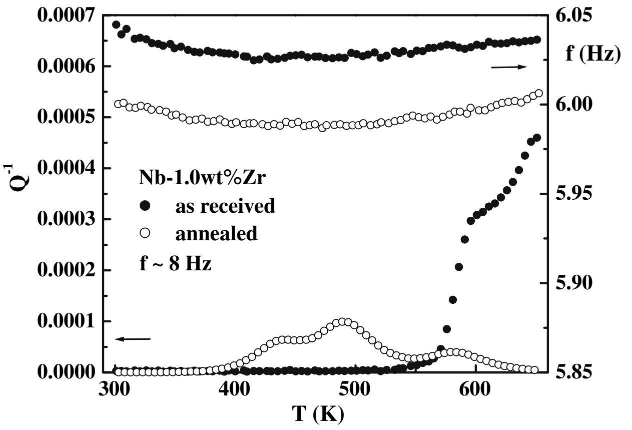

Fig. 2 Internal friction and frequency as a function of temperature for Nb1Zr samples

Anelastic relaxation structures are usually due to elements interstitially present in the crystalline structure. The presence of these relaxation structures after heat treatment can be explained by the fact that elements, such as oxygen and nitrogen, trapped in the inter-grain region migrated to the intra-grain region, due to the grain growth caused by the heat treatment [17]. This peak can be associated with multiple relaxation processes due to the interaction between interstitial solutes and the metallic matrix (Nb–O and Nb–N processes) and between substitutional and interstitial solutes (Zr–O process) [8, 10, 18].

Figure 3 shows the anelastic spectra for samples of the annealed Nb1Zr alloy and with three different quantities of nitrogen in solid solution. In Fig. 3, one can observe that the intensity of the peak increases as the concentration of nitrogen increases.

The interstitial atoms in the bcc lattice form an elastic dipole, which can lie along one of the three cubic axes. The deformation field around an interstitial atom is described by the so-called λ tensor [1]. In alloys with low interstitial concentration (interstitial content <0.01 at %), the observed relaxation structure is fitted with a simple Debye peak [1, 7]. For alloys with high interstitial concentration, relaxation structures are broadened obviously due to interactions among interstitial atoms [1, 19]. Thus, in order to obtain the relaxation parameters for the anelastic spectrum, it is necessary to use computational methods [19].

Taking into consideration that each relaxation process can be represented by a Debye’s type peak [1], internal friction is given by:

$$Q^{-1} = \Delta \frac{\omega\tau}{1 + \omega^2\tau^2} \tag{2}$$

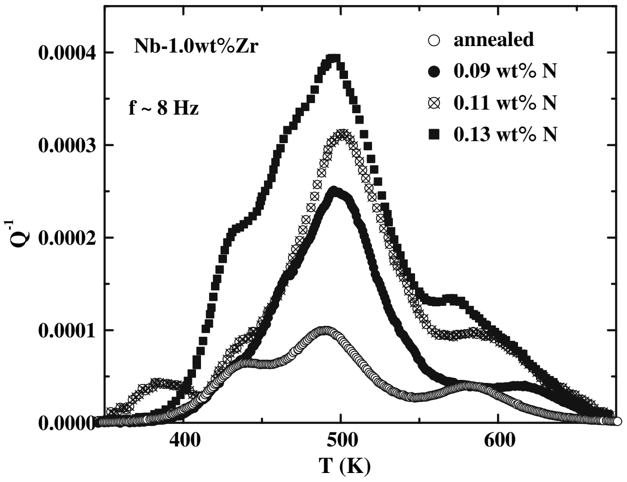

Fig. 3 Mechanical relaxation spectra as a temperature function for Nb1Zr samples, after the nitrogen charge

in which, ω is the system's angular frequency, τ is the relaxation time and Δ is relaxation intensity.

If the relaxation process is thermally activated, its behavior can be described by the Arrhenius' law and it is possible to calculate the relaxation time. Thus, internal friction can be expressed as [1, 20]:

$$Q^{-1} = \frac{Q_m^{-1} T_m}{T} \sec h\left[\frac{H}{k}\left(\frac{1}{T} - \frac{1}{T_m}\right)\right] \tag{3}$$

in which, Q_m^{-1} is maximun internal friction; H is the activation enthalpy, k is Boltzmann's constant and T_m is the peak temperature.

When more than one relaxation process is present, a more complex anelastic spectrum is expected, due to the interaction of interstitial elements with substitutional elements [21–23]. In this case, the anelastic spectrum can be explained by a superposition of several Debye peaks, and internal friction can be expressed as [1, 20]:

$$Q^{-1}(T) = \sum_{i=1}^{n} Q_{mi}^{-1} \frac{T_{mi}}{T} \sec h\left[\frac{H_i}{k}\left(\frac{1}{T} - \frac{1}{T_{mi}}\right) + \ln\left(\frac{f(T)}{f_{mi}}\right)\right] \tag{4}$$

in which, Q_{mi}^{-1} is the peak height, T_{mi} is the peak temperature; H_i is the activation enthalpy; k is Boltzmann's constant; f is the frequency; f_{mi} is the frequency at $T_{mi,}$ and i represents each Debye peak.

The internal friction spectra shown in Fig. 3 were decomposed into the constituent relaxation peaks by using the peak-fitting modulus of the Microcal Origin® software and the results are presented in Figs. 4–7.

The alloy is composed of niobium and zirconium and the analysis of gases shows (see Table 2) that the sample contains a certain amount of oxygen and nitrogen in solid solution. The analysis was started by placing the normal

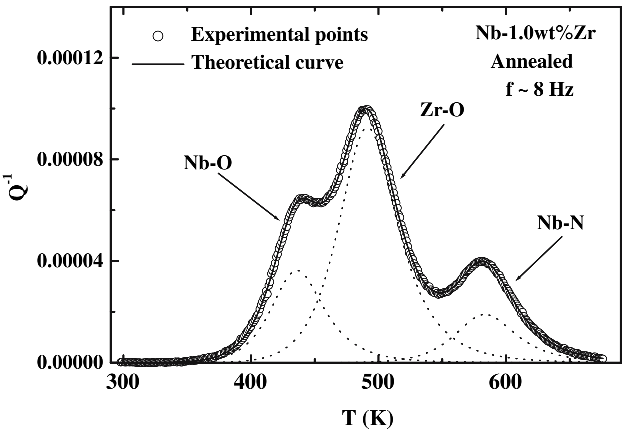

Fig. 4 Constituent relaxation processes of the anelastic spectrum measured at a frequency of around 8 Hz for the Nb–Zr sample after annealing (0.03 wt% N and 0.07 wt% O)

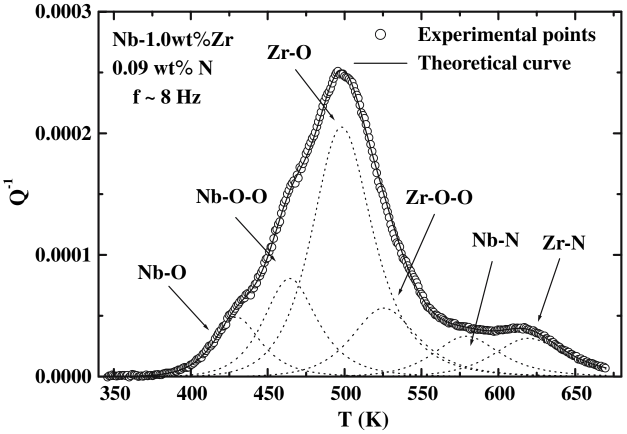

Fig. 5 Constituent relaxation processes of the anelastic spectrum measured at a frequency of around 8 Hz for the Nb–Zr sample with 0.09 wt% N and 0.4 wt% O

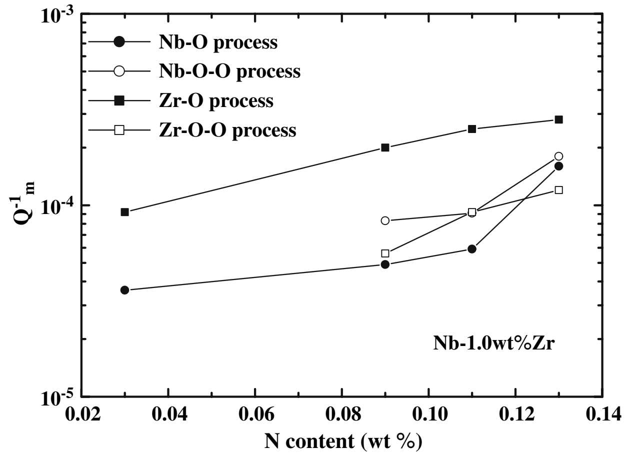

Fig. 6 Variation of peak heights due to oxygen atoms in the Nb1Zr alloy

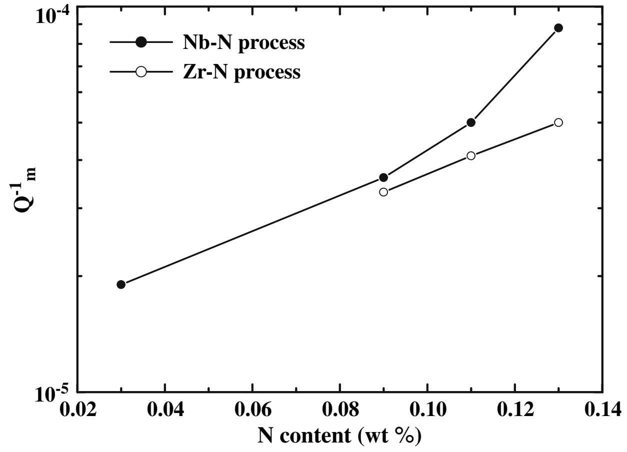

Fig. 7 Variation of peak heights due to nitrogen atoms in the Nb1Zr alloy

Snoek peaks, that is, the relaxation processes, which are due to the stress-induced ordering of oxygen and nitrogen atoms around niobium and zirconium atoms that compose the alloy (Nb–O and Zr–O processes) and due to the stress-induced ordering of nitrogen atoms around niobium atoms of the metallic matrix (Nb-N process). These processes were exhaustively studied in pure metals [2–4, 7, 17–20, 24, 25] as in Nb–Ti and Nb–Zr alloys containing oxygen in solid solution [10, 11, 13, 23, 26–29], and have energy activations of 1.15, 1.22, and 1.52 eV, respectively. The interactions were initiated setting initial temperature, intensity, and frequency values for each peak. The temperature and intensity of each peak are free to vary until the program finds the best values for them, allowing the fitting of the curve, until the correlation index reaches values greater than 0.9999. The activation energy values for the three above-mentioned Snoek peaks were maintained constant, because their values are widely known .

Figure 4 shows the results of peak decomposition for the Nb1Zr measured after annealing, with a correlation index of 0.999995. Three peaks were identified. The first one, at a lower temperature, was attributed to the stress-induced ordering of free oxygen atoms among octahedral sites, around the niobium atom of the metallic matrix; this is the Nb–O Snoek peak. The second process, which is dominant, is located at intermediate temperatures. Since the substitutional zirconium in the Nb–Zr alloy is a strong trapping center for oxygen atoms, [3] it is proposed that this main process is due to the stress-induced ordering of oxygen atoms around the alloy's zirconium atoms; here labeled Zr–O process. The third relaxation, at high temperatures, is ascribed to nitrogen (Nb–N Snoek peak), which represents the alloy's second interstitial impurity content. Due to the low quantity of zirconium and the high chemical affinity between zirconium and oxygen, the Zr–N relaxation process was not observed. The full line in Fig. 4 represents the sum of three Debye peaks (dot lines), which represent the three proposed relaxation processes.

Analysis of the mechanical relaxation spectrum after the first nitrogen charge is shown in Fig. 5. With nitrogen increase, three new peaks are identified and are associated with the stress-induced ordering of oxygen and nitrogen atoms around the niobium and zirconium atoms in the alloy. The full line in Fig. 5 represents the sum of six Debye peaks (dot lines), which represent the six proposed relaxation processes.

The first four peaks must be associated with the jumps of oxygen atoms, although the intensity of these peaks increases with the increase in nitrogen content. The intensity of these first four peaks increases, even though the oxygen content, measured by gas analysis remains constant. This fact can be easily explained by the oxygen atoms trapped in grain boundaries and with the annealing, diffused to the intra-grain regions. Gas analysis measures the total amount of oxygen in the inter-grain as well as the intra-grain regions. The total amount of oxygen remaining constant after three nitrogen charges means that no extra oxygen atoms were introduced into the sample, but the oxygen atoms trapped in the inter-grain region were diffused to the intra-grain regions. The result of the analysis for the sample charged with 0.11 and 0.13 wt% of nitrogen showed the same phenomenology.

The first process, at a lower temperature, is the Nb–O Snoek peak, with activation enthalpy of 1.15 eV, observed in the annealing sample too. The second process (temperature around 460 K), was attributed to the jumps (stress-induced ordering) of clusters O–O around niobium atoms in the metallic matrix, with activation enthalpy of 1.21 eV [19, 24, 27]. Figure 6 plots the intensity of these first two peaks with the nitrogen amount. It is observed that the intensity of the second peak can increase more quickly than the first one, with the nitrogen content (and consequently the oxygen content). As the intensity of the relaxation peak is related to the interstitial content, the fact that the second peak intensity increases faster than the first one, means that this relaxation process is due to stress-induced ordering of clusters O–O around niobium atoms in the metallic matrix.

Cantelli & Zkopiak [28] showed that the interstitial oxygen is completely removed from free solid solution, causing the absence of Nb–O peak. This effect occurs due the fact that the titanium acts as a trapping center for oxygen. Substitutional titanium atoms are remarkably stronger trapping center for oxygen with respect to the zirconium atoms, such that free oxygen atoms exist in the lattice. Owing to this fact, it is proposed by this study that the main process is due to the stress-induced ordering of oxygen atoms around zirconium atoms in the metallic matrix, the Snoek Zr–O process (temperature around 500 K), with activation enthalpy of 1.22 eV [8, 10, 26]. The fourth peak (located around 525 K) was not presented earlier in the literature and this study proposes that this peak is associated with the relaxation process due to the stress-induced ordering of clusters O–O around zirconium atoms in the metallic matrix (Zr–O–O process), with activation enthalpy of 1.26 eV. In this case, due to the fact the zirconium content is less than the niobium content, the intensity of this peak is less than the Snoek zirconium peak, contrary to what happens with niobium in this alloy, as can be observed in Fig. 6.

The intensity of the last two peaks increases with the increase in nitrogen content in the samples, which represents the alloy's second interstitial impurity content, as can be observed in Fig. 7. These peaks were associated with jumps of nitrogen atoms around niobium and zirconium atoms in the metallic matrix. The fifth relaxation peak (located at 550 K) was associated with the relaxation process due to stress-induced ordering of nitrogen atoms around niobium atoms in the metallic matrix (Nb–N Snoek peak), with an activation enthalpy of. 1.52 eV [24, 29]. The sixth and last peaks were associated with the relaxation process due to stress-induced ordering of nitrogen atoms around zirconium atoms in the metallic matrix (Zr–N Snoek peak), with an activation enthalpy of. 1.60 eV [8, 18]. The presence of these two peaks in both, Nb–Ti and Nb–Zr alloys [28] indicate that the nitrogen population is always portioned between mobile and trapped atoms in both alloys. This means that titanium and zirconium atoms are nearly equally effective in trapping nitrogen.

Activation enthalpy for the six proposed processes was fixed, based on the values determined earlier by internal friction experiments (exception for Zr–O–O) [8, 18, 24, 25]. In Figs. 4 and 5, it is possible to observe that the summation of the six proposed relaxation processes is very well adjusted to the experimental curve (correlation indexes are 0.999995 and 0.999994, respectively). This is a very good sign and means that our assumptions are very reasonable.

Due to the fact that the concentration of nitrogen is low when compared to oxygen, the relaxation process is not observed due to the pairs of nitrogen atoms around niobium or zirconium in the alloy (N–N relaxation process). Ahmad and Szkopiak [24], studied pure niobium and only observed a Nb–N process for nitrogen content of 0.09 wt% and a Nb–N–N process for nitrogen content above 0.2 wt%.

Conclusion

Internal friction measurements were performed in the Nb-1.0 wt% Zr alloys, containing 0.09, 0.11, and 0.13 wt% of nitrogen in solid solution. The obtained relaxation spectra were analyzed in terms of their constituent peaks. They were identified and attributed to the stress-induced ordering of oxygen atoms around niobium and zirconium atoms that compose the alloy (Nb–O and Zr–O processes, respectively), with activation enthalpy of 1.15 and 1.22 eV, respectively; stress-induced ordering of clusters of oxygen atoms around niobium and zirconium atoms (Nb–O–O and Zr–O–O processes, respectively), with activation enthalpy of 1.21 and 1.26 eV, respectively; and stress-induced ordering of nitrogen atoms around niobium and zirconium atoms (Nb–N and Zr–N processes, respectively), with activation enthalpy of 1.57 and 1.60 eV, respectively.

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