

Determination of the Oxygen and Nitrogen Interstitial Diffusion Coefficient in Niobium by Mechanical Spectroscopy

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Mechanical spectroscopy measurements have been extensively used in the last decades to obtain information about many aspects of the behavior of solutes in metallic materials. Metals of body-centered cubic lattice that contain heavy interstitial elements (oxygen, nitrogen and carbon) in solid solution, present anelastic relaxation peaks when submitted to cyclic tensions, due to process know stress-induced ordering. Internal friction and frequency as a function of temperature were performed between 300 K and 650 K in a polycrystalline sample of Nb, for three distinct conditions, using a torsion pendulum inverted Kê-type operating in a frequency oscillation between 1 Hz and 10 Hz range, with a heating rate of 1 K/min and pressure lower than 2×10^{-5} mbar. The experimental spectra obtained for each condition of the sample, were decomposed by the successive subtraction method in elementary Debye peaks. The following metal-interstitial interactions were identified: Nb-O and Nb-N for all conditions of the sample. From the anelastic relaxation parameters obtained (relaxation strength, peak temperature, activation energy and relaxation time) and lattice parameter (obtained from x ray diffraction), the determination of the oxygen and nitrogen interstitial diffusion coefficient in Nb was possible, for each condition of the sample.

Keywords: *interstitial diffusion, niobium, internal friction, oxygen, nitrogen*

1. Introduction

When a tension wave is applied in a crystalline material, occur the interaction this tension wave with the defects present in solid, causing the energy loss. The energy loss is due to local motion of some micro-structural unit, such interstitials and substitutional atoms, vacancies and dislocations.

Materials containing solute atoms dissolved interstitially often show anelastic behavior due to a process know as stress-induced ordering. Point defects in solids can give rise to anelastic relaxation provided that the defects behave as elastic dipoles. Elastic dipoles represent atomic defects the produce an anisotropic local distortion of the crystal lattice. Heavy interstitial atoms, such as O, N, or C, in body centered-cubic (BCC) metals induce elastic dipoles with tetragonal symmetry. The stress-induced ordering of the dipoles is the elementary step of interstitial diffusion. One manifestation this anelastic behavior is the internal friction, which was originally described by Snoek¹ in iron (Fe) containing carbon and nitrogen as interstitial solutes.

Mechanical relaxation measurements have been used to obtain information about many aspects of behavior of solutes in metals, for example, matrix-solute interactions¹, interstitial-interstitial and substitutional-interstitial interactions²⁻⁴, interstitial diffusion^{5,6}, etc.

For materials of the BCC lattice, when solute species only jumps between octahedral sites occur, the interstitial diffusion coefficient (D) is described^{5,6}:

$$D = \frac{a^2}{36\tau} \quad (1)$$

where a correspond the lattice parameter of material and τ is the relaxation time.

Several techniques can be used to internal friction measurements⁷⁻⁹, of these the torsion pendulum has been frequently used

to study of the heavy interstitial solute interactions such as carbon, oxygen and nitrogen.

In the present work, internal friction and frequency were measured as a function of temperature in an Nb sample containing oxygen and nitrogen in solid solution, for three different conditions: (A) as received sample, (B) annealed and (C) annealed followed by a treatment in a oxygen atmosphere during three hours.

2. Materials and Experimental Procedure

The polycrystalline sample of Nb was obtained by electron-beam zone melting and was supplied in the form of swaged rod of 3 mm in diameter, by FAENQUIL/Lorena. Samples 50 mm long which had been chemically polished to 1 mm diameter in a mixture of nitric and fluoric acids, were used for the internal friction and x ray diffraction (XRD) measurements.

The values of internal friction and frequency were obtained with a torsion pendulum of the inverted Kê-type¹⁰ which was set to give rise an oscillation frequency between 1 Hz and 10 Hz, with a heating rate of 1 K/min and pressure lower than 2×10^{-5} mbar. The data of oscillation decay were collected automatically by two photodiodes connected to a computer. The internal friction was determined from the amplitude decay, which was determined by ratio of the two measured transit times, the frequency was determined from period of oscillation.

Experimental spectra of anelastic relaxation were obtained for three conditions of the sample: (A) as received sample; (B) annealed sample, during two hours, in a temperature of 1170 K and pressure of 2.5×10^{-8} mbar and (C) annealed followed by a treatment in a oxygen atmosphere during three hours, in a temperature of 1170 K at oxygen partial pressure of 5×10^{-5} mbar. The lattice parameter of

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the Nb sample was determined by XRD (powder method) for each sample condition.

The internal friction curves as a function of temperature were resolved into elemental Debye peaks¹¹ using the method of successive subtraction (in the present work, Peak Fitting Module of Origin was used). The anelastic processes were identified, and the relevant parameters (activation energy, relaxation strength, peak temperature, relaxation time) of each of the process were obtained.

With the anelastic relaxation parameters obtained and lattice parameter, the determination of the oxygen and nitrogen interstitial diffusion coefficient in Nb was possible, for each condition of the sample.

3. Results and Discussion

Experimental spectra of anelastic relaxation as a function of temperature have been obtained for the Nb, for three distinct conditions of sample as described above. The chemical analysis of the interstitial impurities in the metals as-received condition was 0.016 at-% of the oxygen and 0.015 at-% of the nitrogen.

XRD spectra revealed only peaks related to the cubic structure for all conditions for the Nb sample. The results obtained from XRD for lattice parameter for each condition of sample were following: (A) $a = (3.295 \pm 0.001) \text{ \AA}$, (B) $a = (3.301 \pm 0.002) \text{ \AA}$ and (C) $(3.297 \pm 0.001) \text{ \AA}$.

Figure 1 shows experimental spectrum of anelastic relaxation of Nb sample, as received (A), that were resolved into two constituent peaks of Debye corresponding to the interactions Nb-O, and Nb-N. These data were obtained oscillation frequency of 4.0 Hz (at room temperature). Other measurements were carried out at this sample using oscillations frequency about 1.4 Hz, 2.8 Hz, 2.9 Hz and 4.1 Hz (at room temperature). The increase of internal friction background is associated of plastic deformation of the Nb sample.

Figure 2 shows the internal friction and oscillation frequency as a function of temperature for the Nb sample, after annealing during two hours at 1170 K and pressure of 2.5×10^{-8} mbar (B). This experimental spectrum of anelastic relaxation was resolved into two elemental Debye peak, associates the matrix-interstitial interactions Nb-O and Nb-N. These data were obtained with an oscillation frequency about 4.1 Hz (at room temperature). Others data were obtained for this condition of the sample using oscillations frequency about 1.4 Hz, 2.4 Hz, 2.9 Hz and 8.2 Hz (at room temperature). After sample annealing, the grown of the internal friction background was attenuated.

Figure 3 shows anelastic spectrum of Nb sample, after annealed followed by a treatment in an oxygen atmosphere during three

hours, in a temperature of 1170 K in oxygen at a partial pressure of 5×10^{-5} mbar (C). These experimental spectrums were decomposed into two relaxation processes, associates the matrix-interstitial interactions: Nb-O and Nb-N, however with the highest relaxation strength which is attributed to the greater amount of interstitial oxygen in solid solution. This data were obtained with an oscillation frequency about 2.9 Hz, and others measurements were carried out using oscillation frequency about 1.4 Hz, 2.4 Hz and 4.1 Hz, these values at room temperature.

Assuming that the peaks are true Debye peaks, one can compute the activation energies (E) for the processes, measuring the width at half of the peak height. Using the condition of Debye peak ($\omega\tau = 1$), have been determined the relaxation time (τ), for each one of relaxation processes. Table 1 shows the parameters of anelastic relaxation for each kind of interaction and all conditions of Nb sample, for oscillation frequency about 4.1 Hz.

The contamination of the Nb sample during annealing is evident, being observed the increase of the intensity of the peaks from Figure 2 and Table 1.

The broadening of oxygen Snoek peak and shift of peak temperature from Figure 3 is associated the increase of interstitial concentration of oxygen due to treatment in an oxygen atmosphere. This indicate the presence of more that one relaxation process, but, according to Povo and Lambri¹² don't exist one physical model that

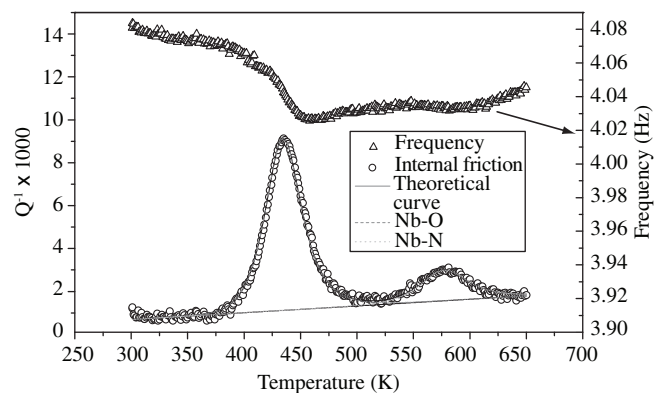


Figure 2. Internal friction and oscillation frequency as a function of temperature for Nb sample, for (B) condition, resolved into constituent peaks corresponding to the interactions: Nb-O and Nb-N.

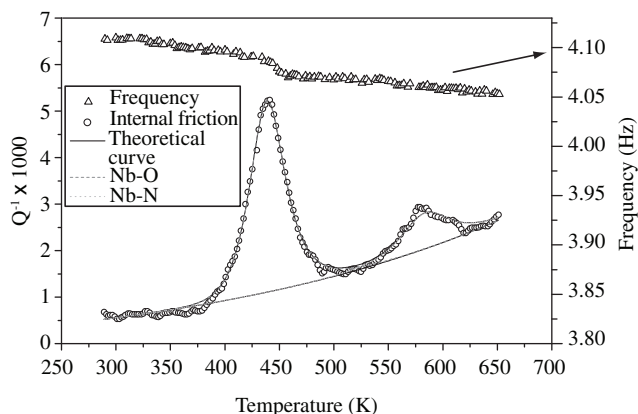


Figure 1. Internal friction and oscillation frequency as a function of temperature for Nb sample, as received, resolved into constituent peaks corresponding to the interactions: Nb-O and Nb-N.

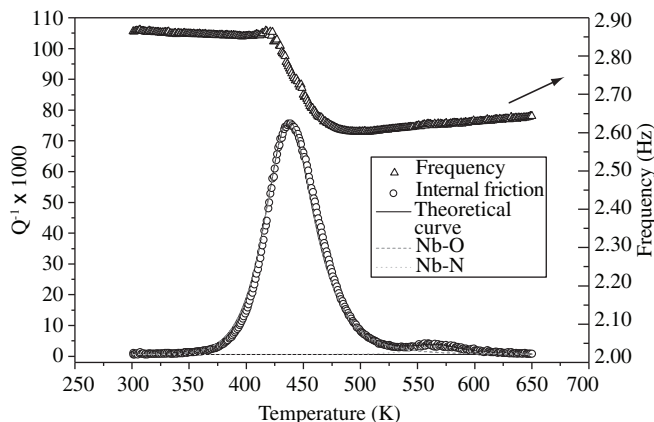


Figure 3. Internal friction and oscillation frequency as a function of temperature for Nb sample, for (C) condition, resolved into constituent peaks corresponding to the interactions: Nb-O and Nb-N.

Table 1. Relaxation rate parameters of Nb-O and Nb-N interactions for (A), (B) and (C) condition of Nb sample, where Q_0^{-1} is background the internal friction spectrum.

Condition	$Q_{\max}^{-1} - Q_0^{-1} \times 10^3$	Interaction	T_{peak} (K)	E (eV)	τ (s)
(A)	4.11	Nb – O	438	1.15	3.895×10^{-2}
	0.78	Nb – N	584	1.52	3.920×10^{-2}
(B)	8.03	Nb-O	435	1.15	3.935×10^{-2}
	1.43	Nb-N	577	1.52	3.946×10^{-2}
(C)	76.42	Nb – O	442	0.90	4.065×10^{-2}
	1.20	Nb – N	570	1.52	4.274×10^{-2}

Table 2. Interstitials diffusion coefficient (D) of oxygen and nitrogen in Nb, for all conditions of the Nb sample.

Condition	T_{peak} (K)	Interaction	$D \times 10^{16}$ (cm ² /s)	$D \times 10^{16*}$ (cm ² /s)
(A)	428	Nb-O	5.332	3.372
	579	Nb-N	5.305	3.567
	438	Nb-O	7.743	6.897
	584	Nb-N	7.694	4.715
(B)	429	Nb-O	4.661	3.627
	570	Nb-N	4.647	2.098
	434	Nb-O	7.692	5.201
	577	Nb-N	7.670	3.186
(C)	437	Nb-O	5.261	6.430
	567	Nb-N	4.970	1.789
	447	Nb-O	9.176	12.777
	575	Nb-N	8.689	2.43

*see G. Horz et al.¹³.

clearly explains feature of multiple peaks of mechanical relaxation in metals of BCC lattice, for high interstitial solute concentration.

Analyzing these results it is possible to estimate the amounts of interstitial elements in solid solution based in the paper of Ahmad and Szkopiak². The estimated values are: 0.018 at-% of oxygen and 0.013 at-% of nitrogen for (A) condition of Nb sample, confirmed the analyses chemical nominal of Nb sample; 0.028 at-% of oxygen and 0.016 at-% of nitrogen for (B) condition of Nb sample and 0.350 at-% of oxygen and 0.015 at-% of nitrogen for (C) condition. Oxygen was analyzed in a TC-436 DR equipment (Leco Co.) and result obtained was (1.18 ± 0.01) at-% of oxygen, this result is regarding total amount of oxygen in the Nb sample.

Interstitial elements in solid solution of metals with BCC lattice are responsible for the Snoek peaks in the relaxation spectrum of internal friction, due to the stress-induced ordering, i.e., diffusion process. Thus assuming that oxygen and nitrogen, for the concentrations present in the Nb sample, they have preferentially octahedral occupation in BCC lattice, can calculate of the interstitial diffusion coefficient of the oxygen and nitrogen in Nb, using the Equation 1. Table 2 shows the interstitial diffusion coefficient of oxygen and nitrogen in Nb, determined from mechanical spectroscopy.

Comparing of results obtained with literature data¹³, the coherence of the find values can be verified, confirmed the validity of technique for determination of interstitial diffusion coefficient, for the limit of solid solution diluted. In Table 2, a small deviation of interstitial diffusion coefficient values can be observed, compared with literature data, for (C) condition of Nb sample. This difference can be explained by double occupation possibility (octahedral and tetrahedral), due to high concentration of interstitial impurities, reported by Boratto and Reed-Hill¹⁴. The region of validity of Equation 1 is the diluted solid solution, which as Ahmad and Szkopiak² this concentration values could be lower at 0.035 at-% for oxygen and nitrogen in niobium.

Other factor that influences the results found is the difference between estimate concentrations in solid solution of oxygen (determined from mechanical spectroscopy) and determined by TC-436 DR equipment (which determine full concentration of impurities), which indicate the formation of precipitated.

4. Conclusions

1. The anelastic relaxation spectra for Nb samples containing different amounts of interstitial elements were obtained as a function of temperature with a torsion pendulum at oscillation frequency in the hertz bandwidth, for three conditions of Nb sample;
2. X ray diffraction revealed only peaks related to the cubic structure for all conditions for the Nb sample, and lattice parameter was determined;
3. The anelastic relaxation spectrum for Nb sample was resolved into two interactions processes: Nb-O and Nb-N, for all conditions; and
4. From the parameters of anelastic relaxation for each kind of interaction (peak temperature, activation energy and relaxation time) and lattice parameter the determination of interstitial diffusion coefficient of oxygen and nitrogen in Nb was possible, for all condition of polycrystalline sample. Being results obtained coherent with literature data, confirmed the validity of technique for determination of interstitial diffusion coefficient, for the limit of solid solution diluted.

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