

## Effect of Impurities on Mechanical Relaxation in Niobium

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Measurements of internal friction as a function of temperature were performed in samples of Nb containing different amounts of substitutional (Zr) and interstitial (O, N) solutes. These data were resolved using the method of successive subtraction, into a series of constituent Debye peaks corresponding to different interactions. For each relaxation process we obtained the height ( $Q^{-1}_{max}$ ) and temperature ( $T_p$ ) of the peak, the activation energy (E) and the relaxation time ( $t_0$ ). The height, shape and temperature of the peaks depend on the concentration of interstitial and substitutional elements. With the addition of substitutional solute one can observe interactions between the two types of solutes (substitutional and interstitial), showing that the random distribution of the interstitial atoms was affected by presence of substitutional atoms. The peaks observed were associated with matrix-interstitial (Nb-O, Nb-N) and substitutional-interstitial (Zr-O) interaction processes.

**Keywords:** *niobium, niobium alloys, interstitial elements, internal friction*

### 1. Introduction

Metals with body-centered cubic (BCC) lattice containing solute atoms dissolved interstitially often show anelastic behavior due to a process known as stress induced ordering. One manifestation of this anelastic behavior is the internal friction ( $Q^{-1}$ ), which was originally observed by Snoek<sup>1</sup> in Fe containing carbon and nitrogen as interstitial solutes in octahedral positions of the type (1/2, 0, 0) and (1/2, 1/2, 0) that produce a strain tensor that has local tetragonal symmetry causing anelasticity.

In the lattices of Nb and Nb-Zr alloys (BCC), oxygen and nitrogen atoms are expected to occupy positions similar to carbon and nitrogen atoms in the Fe lattice.

Several techniques can be used to measure the internal friction<sup>2-5</sup>, of these the torsion pendulum is one which is suitable to the study of metal heavy interstitial solute interactions (such as carbon, nitrogen or oxygen). At low interstitial-solute concentrations, the relaxation strength of internal friction at a given temperature is a function of the nature, positions and concentration of the interstitial atoms.

In the present work the internal friction was measured as a function of temperature in samples of Nb with different amounts of substitutional (Zr) and interstitials (O, N) solutes and were identified matrix-interstitial and substitutional-interstitial interaction processes.

### 2. Experimental Procedure

Nb and Nb-Zr polycrystalline alloys were obtained by electro-beam zone melting and supplied in the form of swaged rods of 3 mm diameter. Nb-Zr single crystal alloys were grown in an electron-beam melting zone apparatus, with an orientation near the center of the standard triangle<sup>6</sup>. The Nb-0.08Zr and Nb-1.48Zr samples were internally oxidized during approximately 70 h at 1270 K in vacuum at a pressure of  $5 \times 10^{-7}$  mbar. Samples 50 mm long, which had been chemically polished to 1.5 mm thickness in a mixture of nitric and fluoride acids, were used for the mechanical relaxation measurements.

These mechanical relaxation values were obtained in the temperature range between 300 and 700 K, using a torsion

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pendulum of the Kê-type<sup>7</sup>, applying a heating rate of 1 K/min, at a pressure near  $10^{-4}$  mbar. A laser beam was deflected by a mirror on the pendulum bar, and data on the decay of the oscillations was collected automatically by two phototransistor connected to a computer. The internal friction was obtained from the amplitude decay.

The internal friction curves as a function of temperature were decomposed into elemental Debye peaks<sup>8</sup> using the method of successive subtraction, and the anelastic relaxation processes was identified comparing the experimental data with literature<sup>9-12</sup>.

### 3. Results and Discussions

Experimental spectra of internal friction as a function of temperature were obtained for the Nb and Nb-Zr alloys. Figure 1 shows the data for the polycrystalline samples Nb and Nb-1.2Zr. Chemical analysis of the interstitial impurities in the metals indicated 50 wt.-ppm of  $O_2$  and 30 wt.-ppm of  $N_2$  in the Nb sample, and 60 wt.-ppm of  $O_2$  and 30 wt.-ppm of  $N_2$  in the Nb-Zr alloys. Comparison of the two curves (Fig.1) indicates that the presence of substitutional element (Zr) modifies the spectra of mechanical relaxation due to the interaction of Zr with the interstitial elements, as such oxygen and nitrogen in solid solution. For unalloyed Nb, the Snoek peaks we observed are Nb-O at 430 K with activation energy of 1.06 eV, and Nb-N at 560 K with activation energy of 1.17 eV<sup>13</sup>. The increase of the values of internal friction at higher temperatures is due to the previous plastic deformation in the samples<sup>14</sup>.

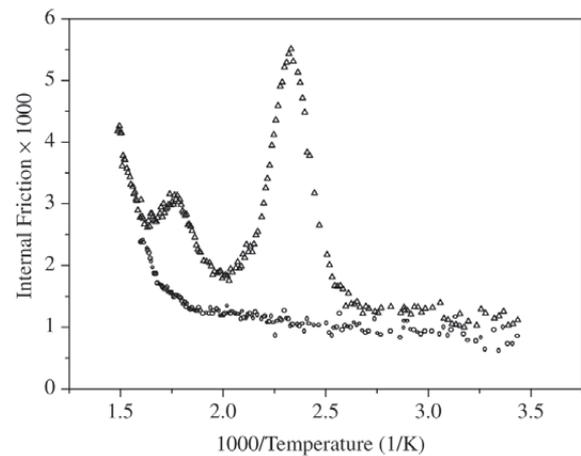
Figure 2 shows the internal friction as a function of temperature for Nb-0.08Zr-O alloy with the experimental relaxation spectrum resolved into four constituent peaks corresponding to the interactions Nb-O (434 K), Nb-O-O (450 K), Nb-O-O-O (490 K) and Zr-O (517 K).

The resolution of internal friction spectra as function of temperature into their constituent Debye peaks was criticized by Weller *et al.*<sup>15-16</sup>. They contested the existence of pairs and triplets of atoms in interstitial solid solution in BCC metals to explain the observed asymmetric broadening of anelastic relaxation peak, and that in the case of high interstitial contents, these atoms would also occupy interstitial tetrahedral positions, resulting in the double occupancy that cause the shifting and broadening of the peak.

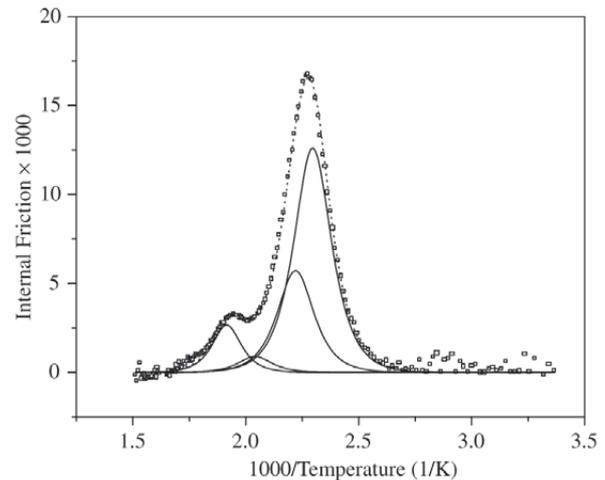
Even using the correction proposed by Weller *et al.*<sup>16</sup> in the results of Fig. 2, for Nb-0.08Zr-O alloy, the asymmetry continued to be evident. This corroborates the existence of more than one process of interaction, in conformity with the results of authors<sup>4,9,10,17</sup>.

According to Povolo and Lambri<sup>18</sup> can be stated that no clear physical model is available to explain all the features of the Snoek relaxation in BCC metals.

Figure 3 shows the experimental spectra for Nb-0.08Zr-O,



**Figure 1.** Internal friction as a function of temperature for unalloyed Nb( $\Delta$ ) and Nb-1.2Zr(O).

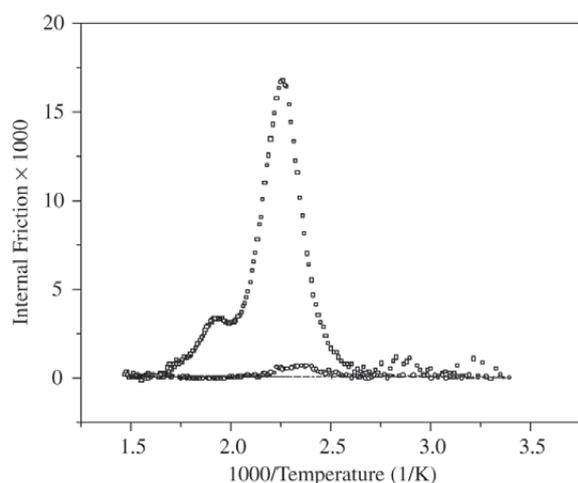


**Figure 2.** Internal friction as a function of temperature for Nb-0.08Zr-O alloy, resolved into constituent peaks corresponding to the interactions: Nb-O at 434 K, Nb-O-O at 450 K, Nb-O-O-O at 490 K and Zr-O at 517 K.

Nb-1.48Zr-O and Nb-0.5Zr single crystals, no mechanical relaxation peak due to the presence of interstitial atoms in solid solution was observed on the Nb-0.5Zr sample, and due to broaden of the relaxation peaks on the Nb-1.48Zr-O it is not possible the decomposition in constituent peaks.

The 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. The height, shape and temperature of these peaks depend on the concentration of interstitial and substitutional elements. The identification of the three con-

stituent peaks Nb-O, Nb-O-O and Nb-O-O-O due to matrix-interstitial interactions was based on the results Ahmad and Szkopiak<sup>9</sup>, and the identification of the Zr-O peak due to substitutional-interstitial interaction was based on results of several authors<sup>10-12</sup>. Assuming that the peaks are true Debye peaks, one can compute the activation energies (E) for the processes, measuring the width at half peak height, and considering that the peaks obey Arrhenius type equation,  $t = t_0 \exp(E/RT_p)$ , it is possible to calculate the



**Figure 3.** Internal friction as a function of temperature for Nb-0.08Zr-O( $\square$ ), Nb-1.48Zr-O( $\circ$ ) and Nb-0.5Zr ( $\bullet$ ) alloys.

relaxation time ( $t_0$ ) for each interaction process. Table 1 shows the parameters of mechanical relaxation for each kind of interaction, compared with values reported in the literature.

The differences observed between the mechanical relaxation parameters obtained for the substitutional-interstitial (Zr-O) interactions and the values reported in literature are probably associated with the existence of ZrO<sub>2</sub> precipitates in the samples<sup>6</sup>. Zirconium additions reduced and broaden the relaxation peaks or even remove them completely, these effects were observed by comparing the internal friction spectra of the Nb-0.08Zr-O alloy with those of the Nb-1.48Zr-O alloy and of the unalloyed Nb and Nb-1.2Zr polycrystalline samples.

#### 4. Conclusions

1. The mechanical relaxation spectra for Nb and Nb-Zr alloys containing different amounts of zirconium were obtained as a function of temperature, where were identified matrix-interstitial and substitutional-interstitial interaction processes.
2. The mechanical relaxation spectra for Nb-Zr single crystals containing different amounts of zirconium and oxygen were obtained as a function of temperature. The spectrum for Nb-0.08Zr sample was resolved into four interaction processes: Nb-O, Nb-O-O, Nb-O-O-O and Zr-O characterizing the mechanical multiple relaxation in the Nb-Zr-O alloys.
3. Comparing the internal friction spectra of the Nb-0.08Zr-O alloy with those of the Nb-1.48Zr-O al-

**Table 1.** Relation rate parameters of Nb-O, Nb-N and Zr-O interactions.

Sample	$Q_{\max}^{-1} \times 10^3$	Interactions	$T_p$ (K)	E (eV)	$t_0$ (s)
Nb	3.8	Nb-O	430	1.06	$1.11 \times 10^{-13}$
	1.8	Nb-N	560	1.71	$1.72 \times 10^{-13}$
Nb-0.08 Zr	12.6	Nb-O	434	1.13	$1.43 \times 10^{-13}$
	5.6	Nb-O-O	450	1.19	$2.38 \times 10^{-13}$
	0.9	Nb-O-O-O	490	1.33	$1.21 \times 10^{-13}$
	2.6	Zr-O	517	1.51	$5.81 \times 10^{-15}$
Nb <sup>9</sup>	-	Nb-O	430	1.15	-
	-	Nb-O-O	443	1.21	-
	-	Nb-O-O-O	473	1.27	-
	-	Nb-N	562	1.51	-
Nb Nb-0.9 Zr <sup>10</sup>	-	Nb-O	417	1.17	-
	-	Nb-O-O	422	1.24	-
	-	Zr-O	483	1.25	-
Nb-1.1Zr <sup>11</sup>	-	Zr-O	483	1.21	-
Nb-1.0 Zr <sup>12</sup>	2.7	Nb-O	430	-	-
	11.2	Zr-O	483	-	-

loy we have observed that zirconium additions really reduce or even remove the relaxation peaks, similarly to the result observed for unalloyed Nb and Nb-1.2Zr polycrystalline samples.

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