Internal Friction Due to Long-Range Diffusion of

Hydrogen in the Nb-46 wt.% Ti Alloy

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The Gorsky Effect was investigated by internal friction measurements in the Nb-46 wt.% Ti-H system. The internal friction measurements were performed in a torsion pendulum with frequency of 3.8 Hz in a temperature range from 80 to 700 K. An interpretation of the experimental data showed that the hydrogen diffusion coefficient D obeys the Arrhenius' law in the temperature interval of 300 to 700 K, with $D_0 = 7.4 \times 10^{-4}$ cm²/s and activation energy $E = (0.102 \pm 0.005)$ eV. At low temperatures, D_o and E were found to be respectively 2.0×10^{-4} cm²/s and (0.063 ± 0.005) eV, with a deviation of the Arrhenius law of higher temperatures.

1. Introduction

The diffusion coefficient for interstitial solutes in metallic systems is determined accurately by Elastic After Effect relaxation measurements, i.e., internal friction, ultrasonic attenuation and acoustic wave dispersion[1,4].

The relaxation by diffusion is based in the lonely condition that the strain field produced by the applied stress (which can be of any symmetry) causes expansion or/and contraction in the crystalline lattice. The dilatation gradient acts as a driving force[3] in each particle, promoting its diffusion. In the strain caused by bending a bar, the solute particles migrate from one side to other side in the sample. In the case of torsion vibration caused in polycrystals with inhomogeneous grain size, it causes radial strain components, making a cylindrical sample to contract and expand radially, enough for diffusion of defects from the center to the surface of the cylindrical sample and vice versa. The diffusion relaxation time τ is directly proportional to the square of the diameter of the sample and inversely proportional to the diffusion coefficient D. The diffusion relaxation time is much higher than the ordering relaxation time and is given approximately by the relation d^2/a^2 (where *a* is the lattice parameter and *d* is the sample diameter)[5].

The torsional modulus G isn't pure in polycrystalline materials with inhomogeneous grains size as in isotropic materials (single crystals). Thus, a compression component of this heterogeneous compression module might exist. The inhomogeneous tension causes compression that give origin to the Gorsky Effect, that is, the G modulus isn't only torsional and it must have a compression component.

The Gorsky Effect due to hydrogen and deuterium long-range diffusion in niobium and vanadium was obtained by elastic after effect and internal friction measurements[4,6]. In spite of hydrogen and deuterium diffusion in metals and alloys being studied by several researchers[4-8], the experimental data are not sufficient to understand the diffusion mechanisms of these atoms in these materials.

The metallic superconductors more thoroughly used in the moment are those that still use niobium and titanium as base materials. All the modern magnets also use Nb-Ti alloys. The great majority of the Nb-Ti superconductors industrially produced uses the Nb-46 wt.% Ti alloy as base material, whose fusion process, of high cost, require precise quality control to prevent the development of composition gradients.

The hydrogen present in this alloy causes embritlement,

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reason why it is of fundamental importance to know the metal-hydrogen interaction mechanisms.

In the present work the Gorsky Effect was investigated by internal friction measurements in the Nb-46 wt.% Ti-H system using a torsion pendulum. The pre-exponential factors and activation energies of hydrogen in this alloy was found and interpolated over a wide temperature range.

2. Experimental Details

The Nb-46 wt.% Ti alloy was produced by Materials Engineering Department of Chemical Engineering Faculty (FAENQUIL), Lorena (Brazil). This alloy was obtained by electron beam zone melting at pressure of less than 10^{-4} Torr. The typical chemical composition of the sample is shown in Table 1[9,10].

The sample was cold-worked starting from a bar 350 mm long and 8 mm in diameter, to 50 mm long and 3 mm in diameter. To use these samples in internal friction measurements by torsion pendulum technique, we had to reduce its diameter to less that 1.5 mm[10]. Our samples were reduced in diameter by chemical polishing using a nitric and fluoridric acid solution.

Measurements were taken on samples at three different conditions: cold-worked; annealed in an ultra-high-vacuum furnace and doped with 0.5 at % of hydrogen. In the second situation, the sample was annealed in a VARIAN model FC 123 UHV furnace at 1073 K and 4.0×10^{-8} Torr vacuum during 4 h. In the third situation, the sample was doped with hydrogen by gas-charge method[11]. The hydrogen equilibrium solubility data for Nb-46 wt.% Ti system used were obtained by Florêncio *et al.*[12-13]. The sample was charged at 1073 K by ninety minutes with 80 Torr of hydrogen partial pressure resulting about 0.5 wt.% of concentration.

The internal friction data were obtained using a torsion pendulum of the inverted Kê type[14], with a heating rate of 1.0 K/min, in a pressure near 10^{-3} Torr and an oscillation frequency of about 3.8 Hz. The oscillation decay data were collected automatically by 2 phototransistors connected to a computer. A laser beam was deflected by a mirror on the pendulum bar and the phototransistors were placed side-by-side in the path of the deflected beam near the center of oscillation so that the beam transit time was inversely proportional to the oscillation amplitude. The internal friction was obtained from the amplitude decay, which was determined by the ratio of the two measured transit time[15].

3. Experimental Results

Figure 1 shows the internal friction as a function of temperature measured at frequency of 3.8 Hz for the Nb-46 wt.% Ti alloy in two conditions, cold-worked and annealed[16]. We can observe the effect caused by annealing.
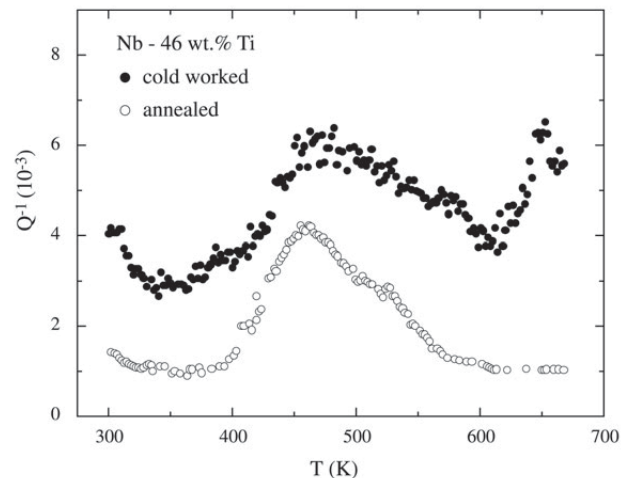
Figure 2 shows the internal friction as a function of temperature for second and third conditions, measured with the same frequency. The lower curve is the annealed sample where we observe a complex relaxation structure composed by several Debye type peaks due to stress induced ordering of oxygen and nitrogen atoms present in the sample around Nb and Ti atoms of the metallic matrix[16,17]. In the upper curve, we observe an increase of the relaxation strength caused by introduction of hydrogen.

Using the same procedure as that of Cantelli *et al.*[4] for flexural vibrations, we show the results obtained in torsion pendulum in the Fig. 3.

4. Discussion

The relaxation theory of diffusion formulated by Gorsky[3] and developed by Alefeld *et al.*[1,2] for cylindrical samples, is given by:

$$Q^{-1}(T) = \frac{\Delta_G}{T} \sum_{n=1,3,5,\ldots} \left\{ \frac{1}{n^4} \left(\frac{2\omega\tau_n}{1+\omega^2\tau_n^2} \right) \right\} \qquad (1)$$

Figure 1. Internal friction as a function of temperature for the Nb-46 wt.% Ti sample, cold-worked and annealed, measured with frequency of 3.8 Hz.

Table 1. Chemical Analysis of the Nb-46 wt.% Ti alloy[9,10].

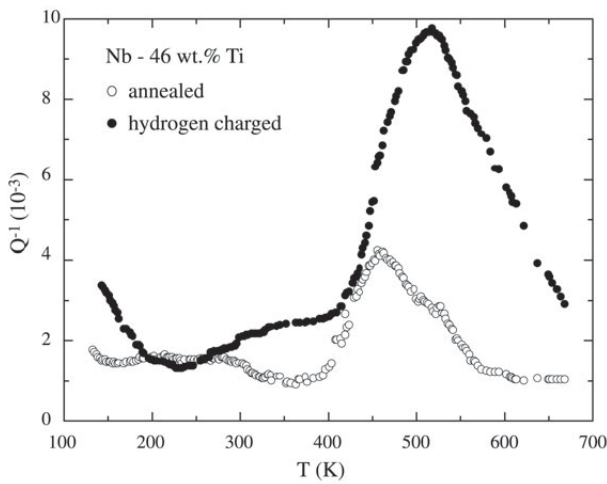| Elements	Ta	Fe	Si	Ni	Cu	Al	O	N	C
Concentration (wt. ppm)	< 500	67	65	93	6	29	500	126	44

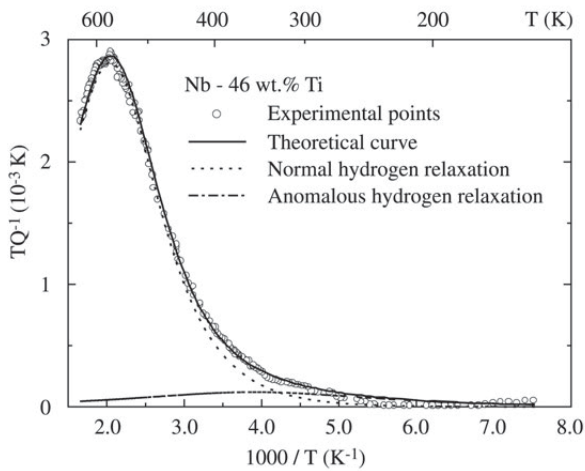where: $\tau_n = \dfrac{d^2}{n^2 \pi^2 D^2}$

d is the sample diameter.

D is the diffusion coefficient of the migrant solute atoms.

Neglecting the contributions of the higher order terms in comparison to the first order term, we have:

$$Q^{-1}(T) = \frac{\Delta_G}{T} \left(\frac{2\omega\tau_1}{1 + \omega^2 \tau_1^2} \right) \qquad (2)$$

Figure 2. Internal friction as a function of temperature for the Nb-46 wt.% Ti sample, annealed and hydrogen charged, measured with frequency of 3.8 Hz.

Figure 3. Internal friction *vs.* the inverse of the temperature for the Nb-46 wt.% Ti sample, due to Gorsky Effect.

where: τ_1 is the diffusion relaxation time obtained by Arrhenius' equation, $\tau_1 = \tau_{01} \exp(E/kT)$, with E as the activation energy of migrant solute atoms and k as the Boltzmann constant.

The relaxation strength Δ_G has different values for the hydrogen diffusion occurring above or below 300 K. $\Delta_{G>}$ is denoted as the relaxation strength at temperatures higher than 300 K and $\Delta_{G<}$ as the relaxation strength at temperatures under 300 K. Thus:

$$\Delta_{G>} = \frac{C_> v_o}{T_{p>}} \frac{(\Delta\lambda)_>^2}{J_u} \qquad (3)$$

$$\Delta_{G<} = \frac{C_< v_o}{T_{p<}} \frac{(\Delta\lambda)_<^2}{J_u} \qquad (4)$$

where: $C_>$ and $C_<$ are the defect concentration at temperatures above or below 300 K, respectively; $T_{p>}$ and $T_{p<}$ are the peak temperature for the peak located at the left or at the right side of 300 K, respectively; V_0 is the unit cell volume; J_u is the unrelaxed elastic constant appropriated and $(\Delta\lambda)_>$ and $(\Delta\lambda)_<$ are the form factor of the migrant defects at temperatures above or below 300 K, respectively.

For constant values of concentration, $\Delta_{G>}$ and $\Delta_{G<}$ are constant. The maximum value is obtained at the peak temperature T_p when $\omega\tau_1 = \omega\tau_{01} \exp(E/kT_p) = 1$. Figure 3 shows the TQ^{-1} *vs.* T^{-1}. The results obtained are shown as a relaxation spectrum composed by two single relaxation peaks. The curve 1, located around 500 K shows the diffusion relaxation of hydrogen through equivalent sites and the curve 2, located around 250 K shows the diffusion relaxation of hydrogen at low temperatures, with relaxation strength 5 % of the curve 1. This small peak is probably due to the hydrogen diffusion in other phase of the Nb-46 wt.% Ti-H alloy, at low temperatures. Using the relations (2) and (3), the diffusion relaxation time as well as the hydrogen diffusion coefficient in the alloy were plotted as a function of inverse of temperature, shown in Figs. 4 and 5 respectively.

The diffusion coefficient is especially strongly reduced bellow 316 K, where a decrease of the activation enthalpy is observed. This low-temperature anomaly, which is yet theoretically unexplained, is an indication for a change of the predominant microscopic diffusion mechanism. We observe that the continuous lines obtained by a linear regression of experimental data determine two diffusion coefficients. These continuous lines show an inflection point around 300 K showing that there are two different diffusion relaxation processes that occur below and above 316 K.

Using the successive subtraction method[16], the complex relaxation structure was decomposed in two peaks and consequently the activation energy of the process was deter-
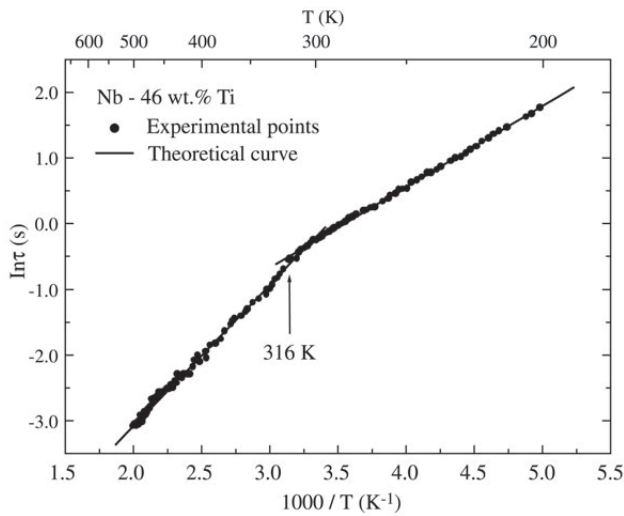
Figure 4. Diffusion relaxation time *vs.* inverse of the temperature for the Nb-46 wt.% Ti sample, due to Gorsky Effect.
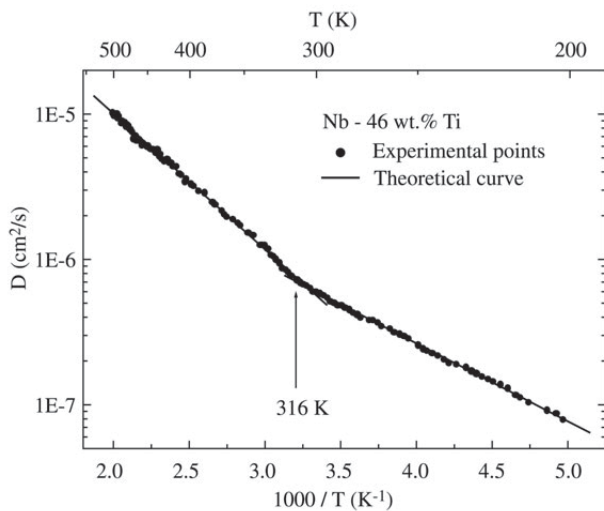
Figure 5. Diffusion coefficient *vs.* inverse of the temperature for the Nb-46 wt.% Ti sample, due to Gorsky Effect.

Table 2. Experimental results obtained by several authors.

System	D_0 (10^{-4} cm^2/s)	E (eV)	T (K)	Ref.
Nb-46 wt.% Ti-H	7.4	0.102	> 300	this work
Nb-46 wt.% Ti-H	2.0	0.063	< 300	this work
Nb-H	5.4	0.109	> 235	4
Nb-H	5.0	0.106	> 300	5
Nb-H	0.9	0.068	< 300	5
Nb-H	5.0	0.106	> 273	7
Nb-H	0.9	0.068	< 273	7

mined. The main results are presented below:

$$E_> = (0.102 \pm 0.005)\ eV$$

$$E_< = (0.063 \pm 0.005)\ eV$$

$$t_{01} = (0.7 \pm 0.2) \times 10^{-3}\ s$$

$$t_{01} = (13.6 \pm 0.2) \times 10^{-3}\ s$$

$$D^> = (7.4 \pm 0.2) \times 10^{-4}\ cm^2/s$$

$$D^< = (2.0 \pm 0.2) \times 10^{-4}\ cm^2/s$$

Our results are very close to those found in the literature[4,6-8], as showed in Table 2. The uncertainty is in the results found at low temperatures. As shown that the relaxation strength of the peak at low temperatures, $\Delta_{G<}$ is about 5% of $\Delta_{G>}$. For this reason, it is not attributed to the same diffusion relaxation process as that of $\Delta_{G>}$. This anomalous peak at 250 K is proposed to explain the break in the diffusion coefficient. It can be attributed to a different diffusion process that occurs when a phase transformation at low temperatures, $\alpha \rightarrow \beta$, occur in such alloy doped with hydrogen[18], probably an association with precipitation effects.

We conclude that the long-range diffusion of interstitial solutes in metallic alloys could be studied by internal friction measurements.

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