Measurement of Oxygen Atom Diffusion in Nb and Ta by Anelastic Spectroscopy

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Impurity interstitial atoms present in metals with BCC structure can diffuse in the metallic matrix by jumps to energetically equivalent crystallographic sites. Anelastic spectroscopy (internal friction) is based on the measurement of mechanical loss or internal friction as a function of temperature. Due to its selective and non-destructive nature, anelastic spectroscopy is well suited for the study of diffusion of interstitial elements in metals. Internal friction measurements were made using the torsion pendulum technique with oscillation frequency of a few Hz, temperature interval from 300 to 700 K, heating rate of about 1 K/min, and vacuum better than 10^{-5} mbar. The polycrystalline Nb and Ta samples used were supplied by Aldrich Inc. The results obtained showed thermally activated relaxation structures due to stress-induced ordering of oxygen atoms around the Nb (or Ta) atoms of the metallic matrix. The results were interpreted by three methods and led to activation enthalpy values for the diffusion of oxygen in Nb and Ta of 1.15 eV and 1.10 eV, respectively.

Keywords: *oxygen diffusion, internal friction, interstitials, Nb, Ta*

1. Introduction

The study of the behavior of group-V metals with interstitials impurities such as O, N, C, H in solid solution has raised many researchers' interest, because these impurities can modify the mechanical properties of these metals[1-3], for example, causing either their softening[4] or hardening[5].

The interactions of these interstitial elements with group-V metals have been largely studied by anelastic spectroscopy measurements (internal friction). The interest in studying bcc metals began with Snoek's early paper[6], in which he postulated a stress-induced ordering of interstitials. Atom reorientation gives rise to pronounced internal friction peaks called Snoek peaks. Such impurity reordering under the action of an applied external force and the interaction with the metallic matrix through a relaxation process is known as stress-induced ordering[7]. The application of this property to diffusion studies is based on the fact that a heavy interstitial atomic element such as oxygen present in a bcc lattice constitutes an elastic dipole with tetragonal symmetry and can produce anelastic relaxation.

Normally, the diffusion coefficient is measured by mass flow technique[8], but in the last thirty years, internal friction measurement has been widely recognized as a very useful technique to study diffusion phenomena in metals and alloys[9]. The discussion of diffusion phenomena in metals and alloys is centered on the fact that an interstitial atom jumps into energetically equivalent sites as a result of the application of external mechanical stress. These jumps give origin to peaks in the internal friction spectra. In general, relaxation peaks in bcc metals appear due to the presence of interstitial solute atoms and are observed as Snoek-type peaks[7]. The relaxation strength and the activation energy of the peaks give some information on the properties of interstitials atoms in bcc metals.

In the last twenty years, the amount of information on relaxation peaks due interstitial oxygen and nitrogen in Nb and Ta has increased sharply[10-14]. The positions of these peaks with respect to temperature are relatively well known, as are the activations energies and the pre-exponential factors[11]. Consequently, peak identification does not present a particular problem. In contrast, some arguments as to whether "clustering" and "anticlustering" occurs with increasing oxygen content[13-19] have been raised. The clustering model proposes the formation of oxygen pairs and other oxygen clusters[13], while the anticlustering model proposes a long-range repulsive interaction between oxygen interstitials and the possibility of some interaction between different types of heavy interstitials, such as oxygen and nitrogen[14].

The purpose of this paper was to study the diffusion of oxygen atoms in Nb and Ta through anelastic spectroscopy measurements as a function of temperature using the torsion pendulum technique. The present investigation determined the activation parameters and the shape of Snoek peaks in Nb and Ta in the presence of oxygen and nitrogen using three methods of data analysis.

2. Experimental Part

Samples of Nb and Ta polycrystals containing oxygen and nitrogen in solid solution were investigated. The samples supplied by Aldrich Inc. had cylindrical form and 60 mm in length by 1 mm diameter, and purity of 99.8% (niobium) and 99.9% (tantalum). The chemical composition of the samples is listed in Table 1.

Anelastic relaxation measurements were made using a torsion pendulum operating with frequency between 0.3 and 10 Hz in the temperature range from 300 to 700 K in vacuum better than 10^{-5} mbar and heating rate of about 1 K/min. The measurement principle is very simple: the sample is made oscillate in its fundamental mode, which causes energy dissipation due to internal friction. In the case of the torsion pendulum, this energy dissipation can be measured directly through the logarithmic decrement in the pendulum oscillation amplitude[7].
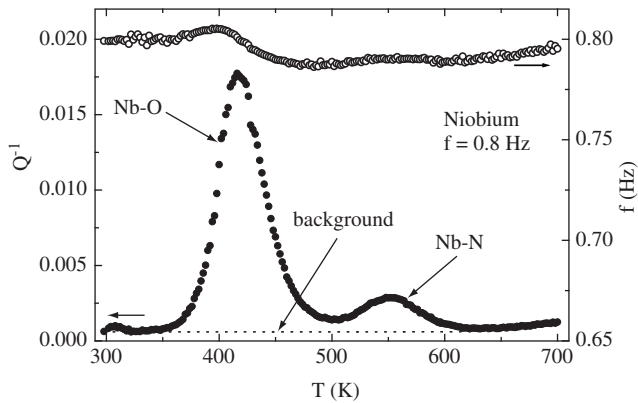
Data relative to the pendulum free oscillation damping are collected automatically using a laser beam reflected by a mirror placed on the pendulum that strikes two phototransistors connected to a microcomputer by a dedicated interface[20].
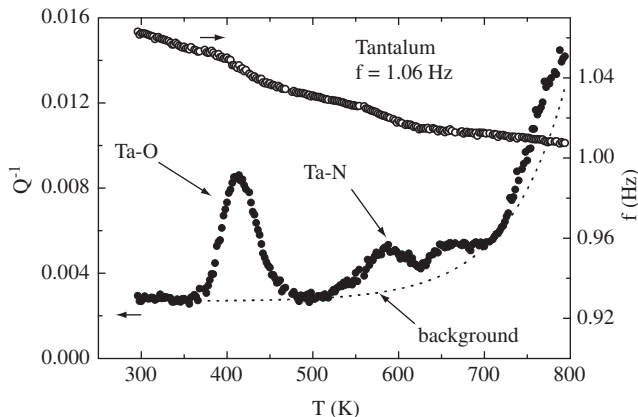
3. Results and Discussion

Typical anelastic spectra for Nb and Ta samples are presented in Figures 1 and 2. The peaks observed in the anelastic spectrum can be associated with the interaction of oxygen atoms (main peak) and nitrogen atoms (secondary peak) with the metallic matrix, Nb(or Ta)-O and Nb(or Ta)-N, respectively. These peaks are very well known and

Table 1. Chemical composition of Nb and Ta samples.

Ta		Nb	
Impurity	Quantity (ppm)	Impurity	Quantity (ppm)
Cu	100	Ta	930
Ni	55	Ti	640
V	15	Na	6
Cr	13	Ni	4
Mg	7	Mg	3
O	35	O	50
N	25	N	30
H	12	H	10

are attributed to the stress-induced ordering of oxygen and nitrogen atoms around Nb (or Ta) atoms in the lattice[10-15]. Figures 1 and 2 also show the behavior of frequency (related with the shear modulus) with temperature. The step in the peak region in the frequency curves shows that they are Snoek type. In this work, analysis will be restricted to the Nb-O relaxation process.

Figures 3 and 4 show the influence of the oscillation frequency on the internal friction spectra for the relaxation process due to stress-induced ordering of the oxygen atoms around Nb (or Ta) lattice atoms. In these figures, it can observed that the relaxation structure (peak) moves to the high temperature zone with the increase in the pendulum oscillation frequency. This effect shows that the relaxation process is thermally activated.
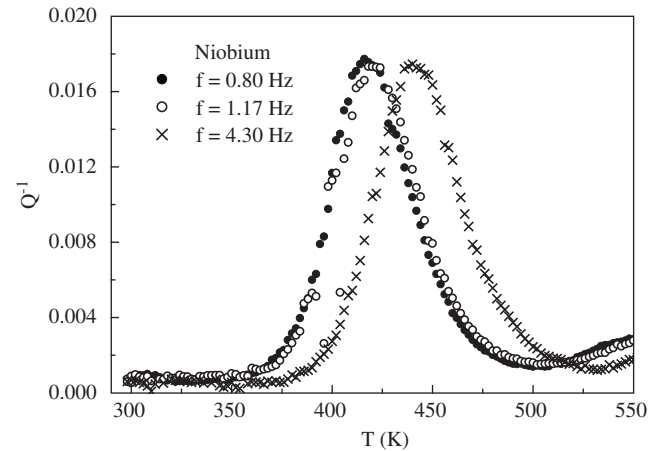
If a single relaxation process governs the relaxation process represented by the peak in the internal friction spectrum, the basic internal friction equation is given by[7]:

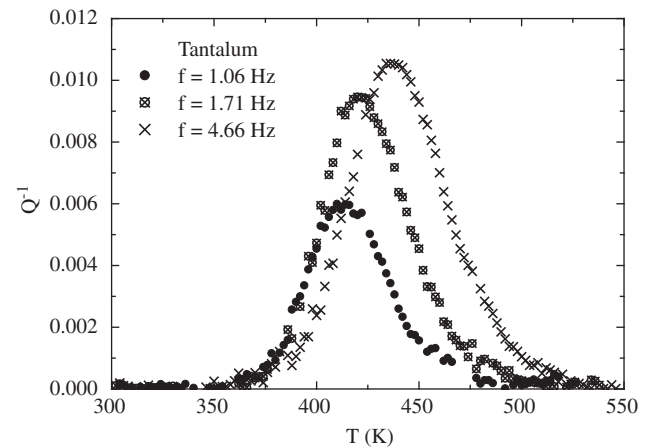$$Q^{-1}(\omega\tau) = \Delta \frac{\omega\tau}{1 + (\omega\tau)^2} \qquad (1)$$

where: Δ is the relaxation strength, τ is the relaxation time, and $\omega = 2\pi f$, f is the pendulum oscillation frequency.

The basic condition for the occurrence of relaxation peaks associated to a single relaxation process is:

$$\omega\tau = 1 \qquad (2)$$

Figure 1. Anelastic relaxation spectrum of Nb measured with frequency of 0.8 Hz.

Figure 2. Anelastic relaxation spectrum of Ta measured with frequency of 1.06 Hz.

Figure 3. Frequency influence on internal friction for Nb-O relaxation process.

Figure 4. Frequency influence on internal friction for Ta-O relaxation process.

Thus, the internal friction and the frequency as a function of the temperature measured in the proximity of Snoek's peak can be used to obtain information on diffusion characteristics of point defects, their thermal activation, the formation of different point defect and their redistribution under the effect of external stress. A point defect produces local distortions in the crystal, and an elastic dipole, a second order tensor, is formed[7].

For a material with bcc structure, the migration of interstitial atoms is given by jumps to energetically equivalent octahedral or tetrahedral sites. The diffusion of these atoms is governed by the following expression[7]:

$$D = \frac{a_0^2}{36\tau} \qquad (3)$$

where: D is the diffusion coefficient, a_0 is the lattice parameter, and τ is the relaxation time.

If the relaxation process is thermally activated, as is the case, the relaxation time can be written using Arrhenius' law[7]:

$$\tau = \tau_0 \exp (H / kT) \qquad (4)$$

where: τ_o is the pre-exponential factor (fundamental relaxation time of the process), H is the activation enthalpy, and k is the Boltzmann constant.

Thus, substituting Equation 4 into Equation 3, we obtain:

$$D = D_0 \exp \left(-\frac{H}{kT}\right) \qquad (5)$$

with:

$$D_0 = \frac{a_0^2}{36\tau_0} \qquad (6)$$

where: D_o is the pre-exponential factor.

Applying logarithm to Equation 5, we obtain:

$$\ln (D) = \ln (D_0) - \frac{H}{kT} \qquad (7)$$

Equation 7 shows that the logarithm of the diffusion coefficient is related with the inverse of temperature. Thus, the logarithmic graph of the diffusion coefficient as a function of the inverse of the temperature gives the activation enthalpy, H, and the pre-exponential factor, D_o.

Substituting Arrhenius' law (Equation 4) in the condition of occurrence of relaxation peak (Equation 2) and applying the logarithm, it is obtained:

$$\ln f = - \ln 2\pi\tau_0 - H / k \, T_p \qquad (8)$$

where: T_p is the relaxation peak temperature.

Thus, the logarithmic graph of the oscillation frequency as a function of the inverse of the temperature gives the activation enthalpy and the fundamental relaxation time of the process. Figure 5 shows the relaxation process graphs for Nb-O and Ta-O. Using linear regression, it can be obtained the relaxation parameters above for the relaxation processes in question. These parameters are presented in Table 2.

Another methodology used to obtain the relaxation parameters of the relaxation processes above was proposed by Weller et al.[11]. It consists in the resolution of Equation 1 for τ, that is:

$$\tau = \frac{1}{\omega}\left[\frac{\Delta}{2Q^{-1}} \pm \sqrt{\left(\frac{\Delta}{2Q^{-1}}\right)^2 - 1}\right] \qquad (9)$$

According with Weller et al.[11], Δ can be written as:

$$\Delta = \frac{2Q_p^{-1} T_p}{T} \qquad (10)$$

where: Q_p^1 is the maximum internal friction, i.e., the internal friction for T_p.

Thus:

$$\tau = \frac{1}{\omega}\left[\frac{Q_p^{-1} T_p}{Q^{-1} T} \pm \sqrt{\left(\frac{Q_p^{-1} T_p}{Q^{-1} T}\right)^2 - 1}\right] \qquad (11)$$

Figures 6 and 7 show the diffusion coefficient as a function of the inverse of the temperature for Nb and Ta samples. The pre-exponential diffusion factor of oxygen in Nb and Ta can be obtained using linear regression:

$$D_o \text{ (Nb)} = (3.17 \pm 0.02) \times 10^{-4} \text{ cm}^2/\text{s}$$

$$D_o \text{ (Ta)} = (2.03 \pm 0.01) \times 10^{-5} \text{ cm}^2/\text{s}$$

The activation enthalpy for these relaxation processes obtained by this methodology is presented in Table 2.
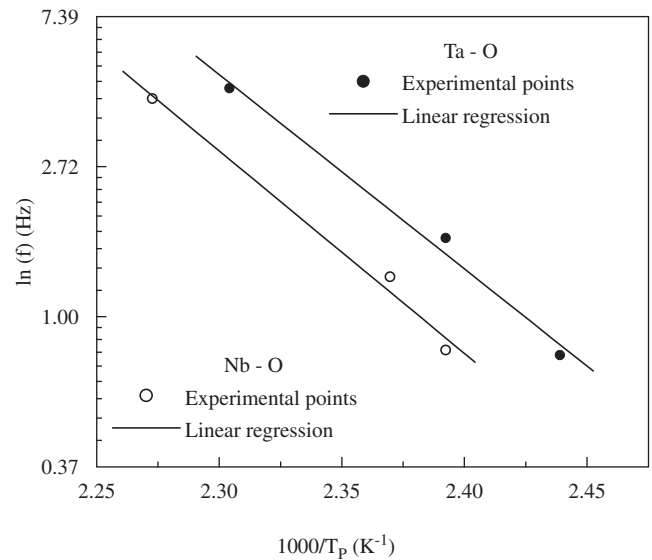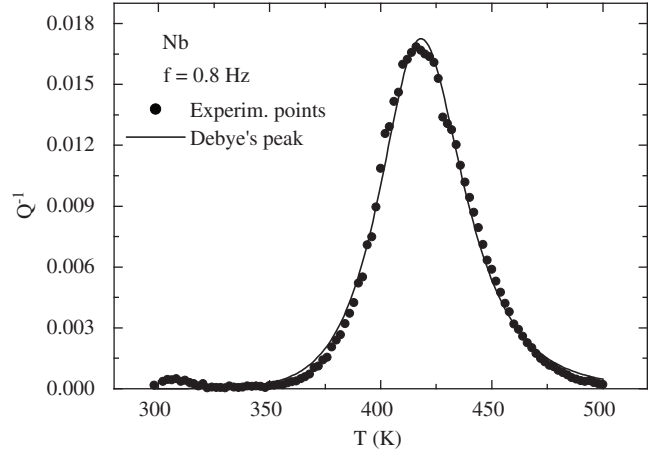

Figure 5. Frequency as a function of the inverse of the peak temperature for Nb-O and Ta-O relaxation processes.

**Table 2.** Relaxation parameters for oxygen diffusion in Nb and Ta.

Process	f (Hz)	T (K)	H (eV)	Ref.
Nb-O			1.02	Figure 5 (relaxation time)
			1.17	Figure 6 (diffusion coefficient)
	0.80	418	1.15	Figure 8 (Debye peak)
	2.9	440	1.15	[10]
	3.5	442	1.17	[15]
	1.0	430	1.15	[17]
	1.3	430	1.15	[19]
	6.0	485	1.15	[22]
Ta-O			0.98	Figure 5 (relaxation time)
			0.91	Figure 7 (diffusion coefficient)
	1.06	414	1.10	Figure 9 (Debye peak)
	1.0	421	1.10	[10]
	1.0	420	1.10	[11]
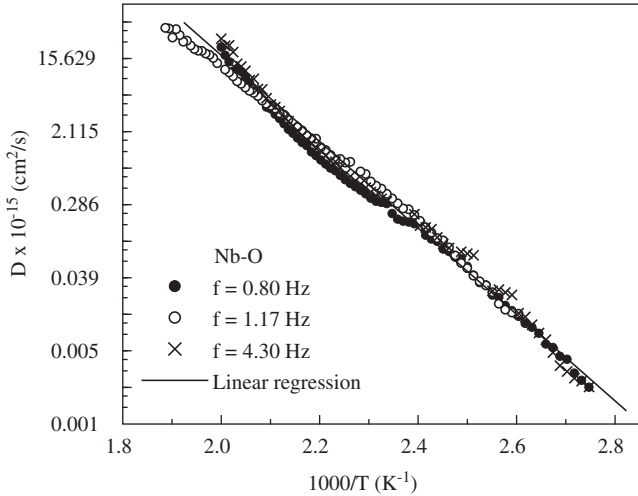
Figure 6. Diffusion coefficient as a function of the inverse of the temperature for Nb-O relaxation process measured with frequencies of 0.80 Hz (•), 1.17 Hz (o), and 4.30 Hz (×).

Figure 8. Internal friction as a function of temperature for Nb sample measured with frequency of 0.80 Hz. The full line shows Debye's peak.
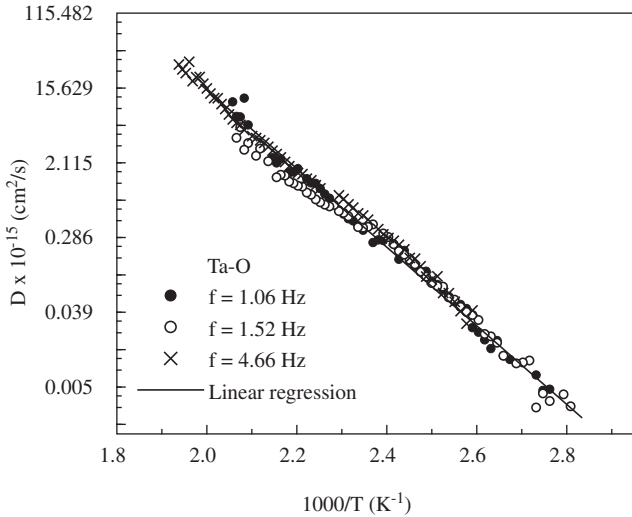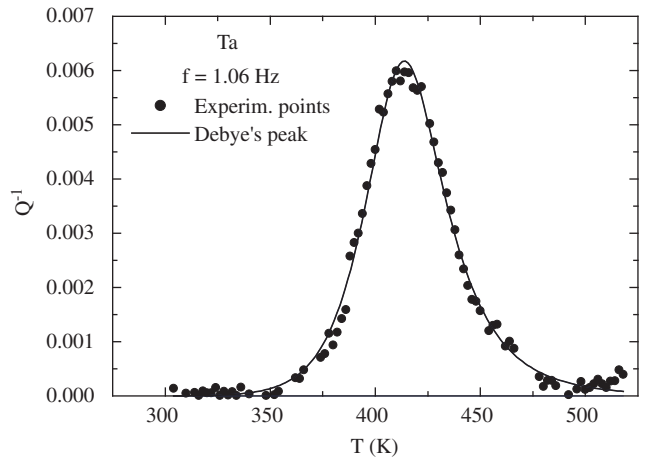

Figure 7. Diffusion coefficient as a function of the inverse of the temperature for Ta-O relaxation process measured with frequencies of 1.06 Hz (•), 1.52 Hz (o), and 4.66 Hz (×).

Figure 9. Internal friction as a function of temperature for Ta sample measured with frequency of 1.06 Hz. The full line shows Debye's peak.

A third procedure consists in using the model proposed by Weller et al.[14] and Equation 1 in combination with Arrhenius' law and the temperature dependence for the relaxation strength Δ. In this case, the internal friction can be written as:

$$Q^{-1}(T) = Q_m^{-1} \frac{T_m}{T} \cosh^{-1} \left[\frac{H}{k_b} \left(\frac{1}{T} - \frac{1}{T_m} \right) + \ln \left(\frac{f(T)}{f_m} \right) \right] \qquad (12)$$

The three parameters that characterize a Debye maximum are Q_m^{-1} (peak intensity), T_m (peak's temperature), and H (activation enthalpy). These parameters can be determined by applying appropriate numerical analytical methods to the experimental data. In this paper, the Peak Fitting Modulus from Microcal Origin®[21] was used.

Figures 8 and 9 show an analysis of one of the curves shown in Figures 3 and 4 based on Equation 12. The theoretical curve (full line) represents a Debye peak. The relaxation parameters are presented in Table 2 too.

The results obtained in this paper are in good agreement with data in the literature on the activation enthalpy of the relaxation

process due to stress-induced ordering of oxygen atoms around Nb and Ta atoms in metallic matrix: 1.15 eV and 1.10 eV, respectively (vide Table 2). These results are based mainly on analysis using Debye peak-based fitting.

Among the three methods presented, analysis by Debye peak-based fitting was the most precise, because the influence of the relaxation process due to nitrogen cannot be discarded by the two other methods, frequency logarithm (Equation 8) and relaxation time (Equation 11). This occurs because the analysis is based on a single relaxation process and the presence of another relaxation process, in this case due the stress-induced ordering of nitrogen atoms, causes a broadening of the main peak.

4. Conclusions

Anelastic relaxation measurements of Nb and Ta polycrystalline samples with oxygen and nitrogen in solid solution were made.

The results showed spectra containing a relaxation peak that was

attributed to the relaxation process due to stress-induced ordering of oxygen atoms around Nb (Ta) atoms in the metallic matrix.

The activation enthalpy and the diffusion parameter values of oxygen atoms in Nb and Ta obtained by three methods were 1.15 eV and 3.17×10^{-4} cm²/s for Nb, and 1.10 eV and 2.03×10^{-5} cm²/s for Ta, respectively.

Acknowledgments

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