Effect of hydrogen, deuterium and oxygen on the anelastic properties of refractory alloys

Lisa H. Brasche

Iowa State University, lbrasche@iastate.edu

Follow this and additional works at: https://lib.dr.iastate.edu/rtd

Part of the Metallurgy Commons

Recommended Citation

https://lib.dr.iastate.edu/rtd/114

This Thesis is brought to you for free and open access by the Iowa State University Capstones, Theses and Dissertations at Iowa State University Digital Repository. It has been accepted for inclusion in Retrospective Theses and Dissertations by an authorized administrator of Iowa State University Digital Repository. For more information, please contact digirep@iastate.edu.
Effect of hydrogen, deuterium and oxygen on the anelastic properties of refractory alloys

Lisa J. H. Brasche

Under the supervision of Otto Buck
From the Department of Materials Science and Engineering
Iowa State University

The effect of hydrogen, deuterium and oxygen on the anelastic properties of V, Nb and V-Nb alloys were examined. Activation parameters were obtained for the oxygen Snoek peak in V and Nb with various hydrogen concentrations. Hydrogen was found not to affect these oxygen relaxation parameters. Thus no interaction of oxygen with hydrogen occurs in the pure metals. Measurement of the hydrogen Snoek peak and the deuterium Snoek peak in V-Nb alloys also led to determination of activation parameters for these interstitials that are consistent with those found by diffusion measurements in this same alloy series. An isotope effect was observed. In addition, oxygen was found not to affect the relaxation of the hydrogen in the V-Nb alloys, indicating that the oxygen-hydrogen interaction in the alloys is also negligible.

1 DOE Report IS-T-1251. This work was performed under contract No. W-7405-Eng-82 with the U.S. Department of Energy.
Effect of hydrogen, deuterium and oxygen on the anelastic properties of refractory alloys

by

Lisa Hager Brasche

A Thesis Submitted to the Graduate Faculty in Partial Fulfillment of the Requirements for the Degree of
MASTER OF SCIENCE

Department: Materials Science and Engineering Major: Metallurgy

Approved:

Iowa State University
Ames, Iowa

1987
TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>ABSTRACT</td>
<td>iv</td>
</tr>
<tr>
<td>1. EFFECT OF HYDROGEN, DEUTERIUM AND OXYGEN ON THE ANELASTIC PROPERTIES OF REFRACTORY ALLOYS</td>
<td>1</td>
</tr>
<tr>
<td>1.1. Introduction</td>
<td>1</td>
</tr>
<tr>
<td>1.2. Theory of Anelastic Response in BCC Metals</td>
<td>2</td>
</tr>
<tr>
<td>1.3. Objectives of this Investigation</td>
<td>4</td>
</tr>
<tr>
<td>2. DEVELOPMENT OF THE VIBRATING REED INTERNAL FRICTION APPARATUS</td>
<td>5</td>
</tr>
<tr>
<td>2.1. Introduction</td>
<td>5</td>
</tr>
<tr>
<td>2.2. Description of the Vibrating Reed Apparatus</td>
<td>5</td>
</tr>
<tr>
<td>2.3. Computerization of the Vibrating Reed Apparatus</td>
<td>10</td>
</tr>
<tr>
<td>2.4. Summary of the Vibrating Reed Capabilities</td>
<td>13</td>
</tr>
<tr>
<td>3. USE OF LINEAR REGRESSION TECHNIQUES IN ANALYSIS OF SINGLE RELAXATION PROCESSES</td>
<td>14</td>
</tr>
<tr>
<td>3.1. Introduction</td>
<td>14</td>
</tr>
<tr>
<td>3.2.1. Sample preparation</td>
<td>17</td>
</tr>
<tr>
<td>3.2.2. Experimental apparatus</td>
<td>18</td>
</tr>
<tr>
<td>3.3. Experimental Results</td>
<td>20</td>
</tr>
<tr>
<td>3.3.1. V+0.2%O</td>
<td>20</td>
</tr>
<tr>
<td>3.3.2. V+0.5%O</td>
<td>25</td>
</tr>
<tr>
<td>3.3.3. Nb+0.2%O</td>
<td>30</td>
</tr>
<tr>
<td>3.4. Discussion</td>
<td>33</td>
</tr>
<tr>
<td>3.5. Conclusions</td>
<td>36</td>
</tr>
<tr>
<td>4. INTERNAL FRICTION SPECTRA OF VANADIUM–NIOBium ALLOYS WITH HYDROGEN, DEUTERIUM OR A COMBINATION OF HYDROGEN AND OXYGEN</td>
<td>38</td>
</tr>
<tr>
<td>4.1. Introduction</td>
<td>38</td>
</tr>
<tr>
<td>4.2. Experimental Details and Data Analysis Procedures</td>
<td>39</td>
</tr>
<tr>
<td>Section</td>
<td>Title</td>
</tr>
<tr>
<td>---------</td>
<td>----------------------------------------------------------------------</td>
</tr>
<tr>
<td>4.2.1.</td>
<td>Sample preparation</td>
</tr>
<tr>
<td>4.2.2.</td>
<td>Use of nonlinear regression procedures in data analysis</td>
</tr>
<tr>
<td>4.3.</td>
<td>Experimental Results and Discussion</td>
</tr>
<tr>
<td>4.3.1.</td>
<td>Hydrogen Snoek peak in V-Nb alloys</td>
</tr>
<tr>
<td>4.3.2.</td>
<td>Comparison of hydrogen effects in V-Nb and amorphous metals</td>
</tr>
<tr>
<td>4.3.3.</td>
<td>Deuterium Snoek peak in V-Nb alloys</td>
</tr>
<tr>
<td>4.3.4.</td>
<td>Effect of oxygen on the hydrogen Snoek peak</td>
</tr>
<tr>
<td>4.3.5.</td>
<td>Coexistence of hydride and hydrogen in solid solution</td>
</tr>
<tr>
<td>5.</td>
<td>CONCLUSIONS</td>
</tr>
<tr>
<td>6.</td>
<td>BIBLIOGRAPHY</td>
</tr>
<tr>
<td>7.</td>
<td>ACKNOWLEDGEMENTS</td>
</tr>
</tbody>
</table>
Effect of hydrogen, deuterium and oxygen on the anelastic properties of refractory alloys

Lisa J. H. Brasche

Under the supervision of Otto Buck
From the Department of Materials Science and Engineering
Iowa State University

The effect of hydrogen, deuterium and oxygen on the anelastic properties of V, Nb and V-Nb alloys were examined. Activation parameters were obtained for the oxygen Snoek peak in V and Nb with various hydrogen concentrations. Hydrogen was found not to affect these oxygen relaxation parameters. Thus no interaction of oxygen with hydrogen occurs in the pure metals. Measurement of the hydrogen Snoek peak and the deuterium Snoek peak in V-Nb alloys also led to determination of activation parameters for these interstitials that are consistent with those found by diffusion measurements in this same alloy series. An isotope effect was observed. In addition, oxygen was found not to affect the relaxation of the hydrogen in the V-Nb alloys, indicating that the oxygen-hydrogen interaction in the alloys is also negligible.

1 DOE Report IS-T-1251. This work was performed under contract No. W-7405-Eng-82 with the U.S. Department of Energy.
1. EFFECT OF HYDROGEN, DEUTERIUM AND OXYGEN
ON THE ANELASTIC PROPERTIES OF REFRACTORY ALLOYS

1.1. Introduction

The characterization of interstitials such as oxygen, nitrogen and carbon in metals has challenged many material scientists (1). Recent development of computer analysis techniques and increased sensitivity in data acquisition, has enhanced data quality and interpretation as was demonstrated at the Eighth International Conference on Internal Friction and Ultrasonic Attenuation in Solids (2). These improvements have lead to increased interest in the interstitials hydrogen and deuterium as well as oxygen, nitrogen and carbon in many materials. Of particular interest in the present study are the properties of hydrogen and deuterium in the solid solution phase of refractory alloys as well as the interaction of hydrogen with oxygen. The general interest in the effects of hydrogen in metals stems from the deleterious effect it can have on mechanical properties (3). It is often difficult, particularly in steels, to distinguish details of the hydrogen interaction with the matrix, dislocations or other interstitials because of low hydrogen solubility. However, in refractory alloys the terminal solubility of hydrogen can be quite large allowing detailed study of these interactions (4).

This thesis examines the anelastic behavior of refractory metals charged with hydrogen, deuterium and oxygen. The thesis is divided into four sections, the first of which contains the introduction, a
short discussion of the theory of anelasticity, and the objectives of this investigation. The major sections cover the use of linear regression procedures to analyze the internal friction peaks due to oxygen in V-0-H and Nb-0-H alloys, development of the vibrating reed internal friction apparatus, and the use of nonlinear regression procedures to analyze V-Nb-H, V-Nb-D and V-Nb-H-0 alloys. A comparison of the present results with results available in the literature as well as a discussion of experimental findings is contained in each section.

1.2. Theory of Anelastic Response in BCC Metals

Elasticity implies that there is a unique equilibrium value of strain for every stress and the relationship between the two is linear. Unlike in elasticity, in anelasticity the response of strain to a stress is not instantaneous. This implies that for an anelastic material to achieve equilibrium after a mechanical force is applied requires time and the effect is known as anelastic relaxation. The goal of internal friction measurements is to determine the nature of the relaxation.

The use of internal friction to determine relaxation parameters has had wide application to bcc metals (2,5-20). Of particular interest is the Snoek relaxation which is defined as the stress induced reorientation of interstitial atoms in a bcc matrix (1). Snoek proposed that interstitials, specifically carbon and nitrogen in iron, occupy octahedral positions in the host matrix. Because the bcc octahedron is not regular, the interstitials occupy sites of
tetragonal symmetry. Therefore the interstitial atom will behave as a tetragonal elastic dipole. Assuming jumps between nearest neighbor octahedral sites, the relaxation time can be related to the diffusion coefficient, $D$, as

$$D = \frac{a^2}{36\tau} \quad (1.2.1.)$$

where $a$ is the lattice parameter and $\tau$ is the relaxation time. In contrast, for tetragonal occupancy, $D$ is given by

$$D = \frac{a^2}{72\tau} \quad (1.2.2.)$$

For a thermally activated process, the relaxation time is calculated using the Arrhenius relationship

$$\tau = \tau_0 \exp\left(\frac{H}{kT}\right) \quad (1.2.3.)$$

where $\tau_0$ is the pre-exponential factor, $H$ is the activation energy, $k$ is Boltzmann's constant and $T$ is the temperature.

To determine $H$ and $\tau_0$, the internal friction is measured as a function of temperature over the total internal friction spectrum. For a single relaxation process, the internal friction versus $1/T$ will be a Debye peak symmetric about $1/T_{\text{max}}$. This assumes that all jump processes are identical to each other and are governed by one single relaxation time. For single relaxation processes, $H$ and $\tau_0$ are determined utilizing a linear regression procedure based on a method proposed by Weller (9,10). However, often there will be a distribution of pre-exponential factors and/or a distribution of activation energies and the internal friction peak will not be a Debye peak. To determine the shape of the distribution of
relaxation times, a nonlinear regression procedure developed by J.R. Cost (41-44) known as Direct Spectrum Analysis may be used.

1.3. Objectives of This Investigation

The present investigation had as its goal to determine the activation parameters for hydrogen in solid solution in V-Nb alloys. Since the hydrogen peak was found not to be a single Debye peak, a nonlinear regression procedure was used to determine the distribution of H and \( \tau_0 \) for this case (41-44) as well as determine their dependence on hydrogen concentration and V/Nb ratio. In addition the effect of oxygen on the hydrogen response as well as the effect of hydrogen on the oxygen relaxation were to be explored. Since an isotope effect was to be expected, the activation parameters of deuterium were to be studied. Alloys used in the present investigation included the following:

- Nb-0-H
- V-0-H
- 90V-10Nb-H
- 80V-20Nb-H
- 70V-30Nb-H
- 70V-30Nb-D
- 70V-30Nb-0-H
- 60V-40Nb-H
2. DEVELOPMENT OF THE VIBRATING REED INTERNAL FRICTION APPARATUS

2.1. Introduction

Early measurements performed on an inverted torsion pendulum showed that an internal friction peak occurs in the vicinity of 78 K at frequencies of approximately 1 Hz in hydrogen doped vanadium-niobium alloys (20). Since this inverted torsion pendulum system is limited to a frequency range of 0.1 to 4 Hz and temperatures above 78 K, a vibrating reed apparatus was developed to meet the need for an extended temperature range and higher frequencies. Electrostatic means are used for excitation and detection of the response of the vibrating reed. The primary advantages of such a system are low background losses and excellent detection sensitivity (1). Another important advantage is that the system only involves electronic components which makes computerization relatively easy. A description of the development of the apparatus as well as details of the computerization follow.

2.2. Description of the Vibrating Reed Apparatus

A flow chart of the system is shown in Fig. 2.1 while Fig. 2.2 shows details of the sample holder. The sample vibrates in flexure at a series of measurement frequencies, n, such as the fundamental mode and the third harmonic. Fig. 2.3 compares a measurement of the same sample at the two different frequencies. The third harmonic occurs at a frequency 6.2626 greater than the fundamental mode in this system. For the alloys chosen and the given sample
Flow Chart for Vibrating Reed Apparatus

Fig. 2.1. Electrical components of the vibrating reed apparatus.
SAMPLE APPARATUS

electrical shield
SAMPLE
detection electrode
to oscilloscope
spring holder
drive electrode
carbon glass thermometer
copper plate
clamps
to multivolt meter
from hi voltage power supply

Fig. 2.2. Details of the sample holder.
Fig. 2.3. Measurement of the internal friction of 70V30Nb charged with 0.55% hydrogen at two frequencies. These are the actual data points without any background subtraction.
configuration, the two measuring frequencies were approximately 250 and 1500 Hz. The sample is a 75 mm long rod with a diameter of 1 mm. The rod is clamped at one end, while the other end is driven by the electric field between a copper electrode and the sample. The input voltage ranges from 5 to 250 volts A.C., depending on the damping of the sample. A second electrode detects the signal which is in the millivolt range. The signal then is amplified, filtered and processed at a digital storage oscilloscope and lock-in amplifier.

The sample is excited such that it vibrates at its resonance frequency. The lock-in amplifier takes the input signal and electronically matches it against the output signal. When these two signals are 180 degrees out of phase, the sample is at the resonance frequency and maximum vibration amplitude is attained. The 180 degree phase shift is a consequence of two separate 90 degree phase shifts. The first 90 degree shift occurs on the drive side which is caused by the displacement of the reed lagging behind the driving force. The remaining 90 degree shift occurs on the detection side and results from the lag between the current and the voltage due to the capacitance. The lock-in amplifier allows a constant amplitude to be easily maintained while insuring the signals are 180 degrees out of phase. Although the vibration amplitude does not affect the hydrogen Snoek peak, amplitude may be important in other internal friction phenomena. The resonance frequency can be changed by changing the sample diameter or by adjusting the length of the reed.
To generate a free decay signal, input power is removed from the drive side while the sample is at resonance. A Nicolet 3091 digital storage oscilloscope is used to capture the free decay signal. The signal is then read into the computer using a standard RS 232 interface where it is analyzed for logarithmic decrement and frequency.

To insure low background damping and to minimize noise the sample clamps are mounted on a copper plate which sits on springs. The copper plate also acts as a heat sink allowing a minimum temperature of 25 K. A model 1020C Cryodyne cryocooler is used to attain these temperatures. A multimeter is used to measure the resistance of a carbon glass thermometer. The thermometer resistance has been calibrated with respect to temperature from 4.2 to 320 K. At present the system is limited to the temperature range of 25 K to room temperature.

2.3. Computerization of the Vibrating Reed Apparatus

Computerization of the vibrating reed apparatus was accomplished using a PDP-11 computer manufactured by Digital Corporation. The stored free decay signal is transmitted to the computer through an RS 232 interface. The frequency and logarithmic decrement are determined by a FORTRAN program as discussed below.

The envelope of the free decay of a natural vibration obeys the following equation:

\[ A(t) = A_0 \exp(-ft) \]  \hspace{1cm} (2.3.1.)

where \( A \) is the amplitude as a function of time, \( t \), \( A_0 \) is the
amplitude at t equal to zero, f is the resonant frequency, and δ is the logarithmic decrement. The internal friction, \( Q^{-1} \), is related to \( δ \) and the amplitudes through the following equation:

\[
Q^{-1} = \frac{δ}{nπ} = \frac{\ln(\frac{A_0}{A_n})}{nπ} \tag{2.3.2}
\]

where \( n \) is the number of cycles. Taking the natural log of equation 2.3.1. generates a straight line described by the following equation:

\[
\ln A(t) = \ln(A_0) - ftδ \tag{2.3.3}
\]

The amplitude of the free decay signal is measured as a function of time. The frequency is calculated as half the number of zero crossings divided by the time from \( A_0 \) to \( A_n \). A linear regression procedure performed on the decaying waveform is used to determine the slope which is proportional to the internal friction. Computerization of the apparatus increased the number of points that could be taken per measurement as well as generating more accurate internal friction and modulus related data. The computerized system allows determination of the frequency as a function of temperature. Since frequency squared is proportional to the elastic modulus, determination of the relative change of modulus with temperature is also obtained. A comparison of computer generated to noncomputerized internal friction data is shown in Fig. 2.4.
Fig. 2.4. Comparison of computerized results to those taken without the use of the computer on the 60V40Nb alloy charged with 2.1% hydrogen. Note the increased number of points measured when using the computer.
2.4. Summary of the Vibrating Reed Capabilities

1. Use of the drive and detection system provides a frequency range of 150-250 Hz as well as a range of frequencies about a factor of 6.26 larger (third harmonic) and over a temperature range of 25 to 300 K.

2. At present, the maximum damping in this system corresponds to a $\xi$ value of $100 \times 10^{-4}$. Higher damping values could be achieved by employing a voltage supply with larger peak to peak amplitude.

3. Computerization of the vibrating reed apparatus lead to more accurate measurement of internal friction and modulus data.
3. USE OF LINEAR REGRESSION TECHNIQUES
IN ANALYSIS OF SINGLE RELAXATION PROCESSES

3.1. Introduction

Internal friction techniques provide a method to determine activation parameters for stress induced jumps of interstitial atoms. The relaxation parameters, activation energy, $H$, and pre-exponential factor, $\tau_0$, determine the relaxation time, $\tau$, as a function of temperature through the Arrhenius equation:

$$\tau = \tau_0 \exp\left(\frac{H}{kT}\right) \quad (3.1.1.)$$

Common methods to determine $H$ and $\tau_0$ involve the use of several measuring frequencies ($f$) which yield a different peak temperature, $T_{\text{max}}$, for each frequency. The slope of the $\ln(f)$ versus $1/T_{\text{max}}$ plot yields the activation energy, $H$. As pointed out by Weller et al. (9,10) however, the same information about the activation parameters can be derived from each individual internal friction curve as discussed below.

For a single relaxation process, the internal friction, $Q^{-1}$, is given as:

$$Q^{-1}(\omega \tau) = \Delta \left[ \frac{\omega \tau}{1 + (\omega \tau)^2} \right] \quad (3.1.2.)$$

which defines the internal friction as a Debye peak centered at $\omega \tau$ equal to one where $\omega$ is the frequency in radians and $\Delta$ is the relaxation strength. Alternatively, equation 3.1.2. can be written as

$$Q^{-1} = \frac{\Delta}{2 \cosh[\ln(\omega \tau)]} \quad (3.1.3.)$$
Substituting 3.1.1. into 3.1.3. and assuming $\Delta$ is constant and that $\omega \tau$ equals 1 at $T_{\text{max}}$, $Q^{-1}$ can be written as a function of temperature given by

$$Q^{-1} = \frac{\Delta}{2 \cosh \left[ \frac{H}{k} \left( \frac{1}{T} - \frac{1}{T_{\text{max}}} \right) \right]}$$

(3.1.4.)

where $Q^{-1}$ versus $1/T$ will be a symmetrical curve centered at $1/T_{\text{max}}$. Combining equations 3.1.1. and 3.1.4. leads to the temperature dependence of $\tau$ given by

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

(3.1.5.)

Because $\Delta$, the relaxation strength, is temperature dependent, the approximation $\Delta = 2Q_{\text{max}}^{-1} T_{\text{max}}/T$ was used. This approximation is the result of substituting $\omega \tau$ equal to one in equation 3.1.2. and solving for $\Delta$ as a function of temperature. Note that values of the relaxation strength listed in the literature are given as % solute while relaxation strength here is related to the peak height and changes with interstitial concentration. The measured internal friction values are then used to generate $\ln(\tau)$ versus $1/T$ plots as seen in Fig. 3.1. The slope of the line is proportional to $H$ and the intercept is equal to $\tau_0$, the pre-exponential factor. A linear regression procedure was used to analyze $\ln(\tau)$ versus $1/T$ data to determine $H$ and $\tau_0$ in $V+0.2\%0$, $V+0.5\%0$ and $Nb+0.2\%0$ alloys. Discussion of the results of this analysis follows.
Fig. 3.1. $\ln(\tau)$ versus $1/T$ for the V-0.2 O-0.18 H alloy. The slope of the linear regression line shown was used to determine the activation energy and $\tau_0$. For this sample and frequency $H$ equals 1.15 eV and $\tau_0$ equals $3.4 \times 10^{-14}$ sec.
3.2. Analysis of the Oxygen Snoek Peak
In V-0-H and Nb-0-H Alloys

In a collaborative effort, internal friction measurements were made using an inverted torsion pendulum on a series of V-0-H and Nb-0-H alloys to determine if hydrogen affects the oxygen Snoek peak. A linear regression procedure, as discussed in 3.1., was then used to determine activation parameters. Oxygen concentrations of 0.2%\textsuperscript{2} and 0.5% were used. A brief discussion of the results and their implications follows as well as a description of the experimental apparatus and sample preparation.

3.2.1. Sample preparation

Internal friction spectra of V+0.2\%O and Nb+0.2\%O were measured by C.V. Owen and H. Indrawirawan, respectively. The internal friction specimens were 75 mm wires of 1 mm diameter. The 0.2\% O samples were swaged from material previously used for tensile specimens to a final diameter of 1 mm (21). The wires were annealed for 2 hours at 1273 K to relieve cold work.

The V+0.5\%O alloys were specially prepared and measured by the author. A vanadium rod of 2.54 mm diameter was charged with 99.95\% pure oxygen gas in a Sieverts type apparatus. The rod was then held at 1573 K for 5 1/2 hours to allow the surface oxide to dissolve and the oxygen to diffuse into the bulk material. This was followed by

\textsuperscript{2} All interstitial concentrations are given in atomic percent.
swaging the rod to a 1 mm diameter and annealing at 1273 K for 1 hour.

Hydrogen charging of the V+0.2% and V+0.5% alloys was achieved using a standard Sieverts type apparatus. The samples were heated to 1273 K under a dynamic vacuum of 10^{-7} torr. The chamber was then cooled to 1123 K and isolated from the pumping system. Hydrogen from thermal decomposition of uranium hydride (UH₃) was admitted at predetermined pressures. The closed system was held at 1123 K for 2 1/2 hours followed by furnace cooling.

Hydrogen charging of the Nb+0.2% alloys was performed by H. Indrawirawan. The samples were heated to 1073 K under a vacuum of 10^{-3} torr and then isolated from the pumping system. Hydrogen gas of 99.95% purity was admitted at a predetermined pressure. The system was held for one hour at 1073 K, 973 K, and 873 K followed by 24 hours at 773 K. The system was then allowed to furnace cool to room temperature.

3.2.2. Experimental apparatus

All internal friction measurements were performed on the inverted torsion pendulum (1). The wire is vibrated in the torsional mode to a predetermined amplitude. It is then allowed to free decay and the free decay signals are recorded as shown in Fig. 3.2.

The internal friction is calculated using the following equation

\[ Q^{-1} = \frac{1}{n \nu f} \ln \left( \frac{A_0}{A_n} \right) \]  

(3.2.1.)

where \( A_0 \) is the initial amplitude and \( A_n \) is the amplitude after \( n \)
Fig. 3.2. Free-decay signal as generated by the inverted torsion pendulum.
cycles at a frequency $f$ in Hz as a function of temperature from 300 K to 600 K. The internal friction values were then substituted into equation 3.1.5. to generate $\tau$ values as a function of temperature.

3.3. Experimental Results

Internal friction of refractory metals alloyed with oxygen has been measured by many researchers (5-20). The goal of the present investigation was to determine if hydrogen has any effect on the oxygen relaxation in these metals. Internal friction of V+0.5%O$^3$, V+0.2%O$^4$, and Nb+0.2%O$^5$ with varying hydrogen concentrations was measured and a linear regression procedure used to calculate the activation parameters. Prior to the linear regression analysis, the background was subtracted from the data of each alloy and all curves normalized to the same $O^{-1}_{\max}$. The results of each alloy system are discussed below.

3.3.1. V + 0.2% O

The effect of hydrogen on the oxygen Snoek peak in vanadium was examined in a vanadium alloy containing 0.2% oxygen. Hydrogen concentrations were chosen such that the O/H ratios would be about

---

3 Measured by the author.
4 Measured by C.V. Owen.
5 Measured by H. Indrawirawan.
0.5, 1.0 and 2.5. Analysis of the data included use of a linear regression procedure with results given in Table I.

Note that the 0.11% hydrogen sample had an unusually high $Q^{-1}_{\text{max}}$, indicating a probable surface contamination problem. The sample was electropolished and measured a second time yielding a smaller value for $Q^{-1}_{\text{max}}$. This indicates that the sample picked up some oxygen during the hydrogen charging process. However, the $H$ and $\tau_0$ values are still within the experimental range for both the original and electropolished sample.

A frequency analysis was performed on the 0.18% hydrogen sample to provide a comparison of the activation parameters obtained from the linear regression procedure with those obtained from the $\ln(f)$ versus $1/T_{\text{max}}$ procedure. The $\ln(f)$ versus $1/T_{\text{max}}$ plot for this sample is shown in Fig. 3.3. $H$, as taken from the slope of this line, is 1.14 (+/- 0.04) eV which is within the range of the linear regression calculation which gave a value of 1.16 (+/- 0.03) eV. Fig. 3.4 shows the normalized $Q^{-1}$ versus $1/T$ curves for each of the three frequencies. Note the data points agree quite well with the theoretical curves.

In the inverse temperature plot, a single relaxation process will be symmetrical about $1/T$. The asymmetry of each measurement is given in Table I where values less than one indicate broadness on the high temperature side. While broadness on the high temperature side appears to be the trend, a correlation between asymmetry and hydrogen concentration does not exist. As will be discussed in the $V+0.5\%$ oxygen case, some nitrogen contamination is possible although
Table I. Data for the Oxygen Snoek peaks in the Vanadium + 0.2 % O, doped with various amounts of hydrogen. H and \( \tau_0 \) obtained using equations 3.1.1. and 3.1.5.

<table>
<thead>
<tr>
<th>Alloy</th>
<th>( f_m ) (Hz)</th>
<th>( T_m ) (K)</th>
<th>( Q_m^{-1} ) (x 10^4)</th>
<th>H (eV)</th>
<th>( \tau_0 ) (sec x 10^{15})</th>
<th>Asym^a</th>
<th>Peak Width^b</th>
</tr>
</thead>
<tbody>
<tr>
<td>V-0.2 0</td>
<td>1.41</td>
<td>459</td>
<td>219</td>
<td>1.16</td>
<td>21</td>
<td>1.02</td>
<td>0.97</td>
</tr>
<tr>
<td>V-0.2 0 + 0.11 H</td>
<td>1.40</td>
<td>456</td>
<td>269</td>
<td>1.14</td>
<td>11</td>
<td>0.96</td>
<td>0.98</td>
</tr>
<tr>
<td>+ 0.11 H^c</td>
<td>1.43</td>
<td>459</td>
<td>240</td>
<td>1.19</td>
<td>11</td>
<td>0.96</td>
<td>0.98</td>
</tr>
<tr>
<td>+ 0.18 H</td>
<td>0.33</td>
<td>438</td>
<td>212</td>
<td>1.15</td>
<td>34</td>
<td>0.85</td>
<td>1.05</td>
</tr>
<tr>
<td>+ 0.18 H</td>
<td>0.60</td>
<td>447</td>
<td>210</td>
<td>1.19</td>
<td>12</td>
<td>0.88</td>
<td>1.03</td>
</tr>
<tr>
<td>+ 0.18 H</td>
<td>1.46</td>
<td>461</td>
<td>217</td>
<td>1.14</td>
<td>34</td>
<td>1.03</td>
<td>1.06</td>
</tr>
<tr>
<td>+ 0.45 H</td>
<td>1.44</td>
<td>458</td>
<td>223</td>
<td>1.16</td>
<td>39</td>
<td>0.86</td>
<td>1.04</td>
</tr>
<tr>
<td>V-0.2 0^d</td>
<td>1.46</td>
<td>459</td>
<td>219</td>
<td>1.14</td>
<td>40</td>
<td>1.04</td>
<td>1.03</td>
</tr>
</tbody>
</table>

^aAsymmetry is calculated using the width of the low temperature side divided by the width of the high temperature side taken at half the peak maximum.

^bPeak width is calculated as the actual width of the internal friction peak at half the peak maximum divided by the width if the peak were a Debye peak.

^cSample measurements made after electropolishing.

^dSample measurements made after the 0.45 H sample was extracted.
Fig. 3.3. ln (f) versus 1/T for the V-0.2 O-0.18 H sample taken at frequencies of 0.33, 0.60 and 1.46 Hz. The slope of the linear regression line is proportional to the activation energy and a value of H equal to 1.14 eV was found.
Fig. 3.4. Normalized $Q^{-1}$ versus temperature for the V-0.2 $\Delta$-0.18 H sample was measured at three frequencies. The background has been subtracted from the data. The theoretical Snoek peak is also shown.
this is not evident in Fig. 3.4. Note that the asymmetries are not as large as in the V+0.5% oxygen case as listed in Table II.

To determine if hydrogen charging has any effect on the activation parameters, the 0.45% hydrogen sample was extracted. This was accomplished by heating the sample to 1273 K in a dynamic vacuum for one hour. Table I indicates that the results for 0.45% H and for the hydrogen extracted are within the range of H and $\tau_0$ expected. Fig. 3.5 contains the data points for the V+0.2%0 without hydrogen, with 0.45% hydrogen and with 0.45% hydrogen extracted. Note the agreement with the theoretical curve for all compositions. This indicates the hydrogen addition does not affect the peak shape or activation parameters as will be discussed in Section 3.4.

3.3.2. V+0.5%

The higher oxygen concentration, 0.48% oxygen, lead to a $Q^{-1}_{\text{max}}$ that was greater than $500 \times 10^{-4}$. Damping values of this magnitude are difficult to resolve with the present inverted pendulum system. As seen in Fig. 3.6, the top of the peak is "cut off". Since the true value of $Q^{-1}_{\text{max}}$ is not known, a value of $570 \times 10^{-4}$ was estimated as the most probable $Q^{-1}_{\text{max}}$. This value is based on the half width of a single relaxation peak with H equal to 1.16 eV. It assumes the oxygen concentration is the same for all four samples.

Internal friction versus $T^{-1}$ is plotted along with the theoretical curve for H equal to 1.16 eV in Fig. 3.7. Note that the scatter is considerable on the high temperature side compared to the low temperature side. There also appears to be a peak coming in at
Fig. 3.5. Normalized $Q^{-1}$ versus $1/T$ for the V-0.2 O alloy prior to hydrogen charging, charged with 0.45% hydrogen and with the hydrogen extracted. The background has been subtracted from the data. The theoretical Snoek peak is also shown as a solid line.
Fig. 3.6. $Q^{-1}$ versus temperature for the V-0.48 O-0.48 H alloy. The peak temperature is 460 K for this alloy and the maximum $Q^{-1}$ should be approximately 600 compared to 470 on the scale shown.
Fig. 3.7. $Q^{-1}$ versus temperature for the V-0.48 O alloy without hydrogen and with 0.48 hydrogen. Note the high temperature peak is at the correct location for the nitrogen Snoek peak in vanadium.
high temperature. The nitrogen Snoek peak for vanadium occurs at 537 K at a frequency of 0.65 Hz. Asymmetries and peak widths are listed in Table II. Note the asymmetry values are less than one which indicates high temperature broadness. The asymmetry values are much higher than those found in the V-0.20 alloys. The large values given as peak width are probably a result of uncertainty in the actual peak height. The oxygen charging of these samples probably resulted in some nitrogen contamination and the shape of the high temperature side.

Table II. Data for the Oxygen Snoek peaks in Vanadium + 0.48 % O doped with various amounts of hydrogen

<table>
<thead>
<tr>
<th>Alloya</th>
<th>F(Hz)</th>
<th>Asym. b</th>
<th>Peak Widthc</th>
</tr>
</thead>
<tbody>
<tr>
<td>V-0.48 0</td>
<td>0.65</td>
<td>0.96</td>
<td>1.16</td>
</tr>
<tr>
<td>V-0.48 0 + 0.3 H</td>
<td>0.61</td>
<td>0.82</td>
<td>1.11</td>
</tr>
<tr>
<td>+ 0.48 H</td>
<td>0.67</td>
<td>0.69</td>
<td>1.17</td>
</tr>
<tr>
<td>+ 0.57 H</td>
<td>0.66</td>
<td>0.73</td>
<td>1.14</td>
</tr>
</tbody>
</table>

Sample diameter is 1 mm.

Asymmetry is calculated using the width of the low temperature side divided by the width of the high temperature side taken at half the peak maximum.

Peak width is calculated as the actual width of the internal friction peak at half the peak maximum divided by the width if the peak were a Debye peak.
3.3.3. **Nb+0.25%O**

The effect of hydrogen on the oxygen Snoek peak in niobium was examined in Nb-0-H alloys. The results of the linear regression are given in Table III. Hydrogen concentrations were chosen such that O/H ratios would be 0.5, 1.0 and 2.5.

Comparison of the $\nu_{\text{max}}^{-1}$ values indicates a lower oxygen concentration in the uncharged Nb+0.2%O sample than in those charged with hydrogen. Since $\nu_{\text{max}}^{-1}$ is proportional to the oxygen concentration the disparity in peak heights indicates oxygen was picked up during the hydrogen charging. The slight differences in oxygen concentration do not appear to affect $H$ or $\tau_0$.

A frequency analysis was performed on the Nb+0.2%O+0.27%H sample as was done for the V+0.2%O+0.18%H alloy. The frequency analysis resulted in $H$ equal to 1.13 +/- 0.1 eV. While this value is higher than that found from the linear regression (1.12 eV), both values agree with those found in the literature. The asymmetries and peak widths for these alloys are also given in Table III. As in the vanadium case, there is some variation but no correlation with hydrogen concentration. The variation is larger in the Nb+0.2%O alloys than in the V+0.2%O alloys. This is believed to result from possible nitrogen contamination due to the different hydrogen charging procedure. The high temperature sides of the peaks in Fig. 3.8 do show evidence of broadening when compared to the theoretical curves as would result from nitrogen pickup.
Table III. Data for the Oxygen Snoek peaks in the Niobium + 0.25 % O, doped with various amounts of hydrogen. H and $\tau_0$ obtained using equations 3.1.1. and 3.1.5

<table>
<thead>
<tr>
<th>Alloy$^a$</th>
<th>$f_m$ (Hz)</th>
<th>$T_m$ (K)</th>
<th>$Q_m^{-1} \times 10^4$</th>
<th>H (eV)</th>
<th>$\tau_0 \times 10^{15}$</th>
<th>Asym.$^b$</th>
<th>Peak Width$^c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nb-0.25 O</td>
<td>1.33</td>
<td>424</td>
<td>161</td>
<td>1.14</td>
<td>4</td>
<td>1.13</td>
<td>1.07</td>
</tr>
<tr>
<td>Nb-0.25 O + 0.19 H</td>
<td>1.32</td>
<td>422</td>
<td>238</td>
<td>1.10</td>
<td>9</td>
<td>0.96</td>
<td>0.98</td>
</tr>
<tr>
<td>+ 0.27 H</td>
<td>0.27</td>
<td>403</td>
<td>228</td>
<td>1.14</td>
<td>3</td>
<td>0.89</td>
<td>1.11</td>
</tr>
<tr>
<td>+ 0.27 H</td>
<td>0.55</td>
<td>411</td>
<td>229</td>
<td>1.12</td>
<td>7</td>
<td>0.96</td>
<td>1.07</td>
</tr>
<tr>
<td>+ 0.27 H</td>
<td>1.31</td>
<td>423</td>
<td>254</td>
<td>1.10</td>
<td>9</td>
<td>0.98</td>
<td>1.04</td>
</tr>
<tr>
<td>+ 0.65 H$^d$</td>
<td>0.67</td>
<td>414</td>
<td>211</td>
<td>1.09</td>
<td>15</td>
<td>0.89</td>
<td>1.07</td>
</tr>
<tr>
<td>+ 0.65 H</td>
<td>1.30</td>
<td>423</td>
<td>238</td>
<td>1.13</td>
<td>5</td>
<td>0.86</td>
<td>1.09</td>
</tr>
<tr>
<td>Nb-0.25 O$^e$</td>
<td>0.67</td>
<td>413</td>
<td>211</td>
<td>1.09</td>
<td>15</td>
<td>0.82</td>
<td>1.07</td>
</tr>
</tbody>
</table>

$^a$Sample diameter is 1 mm except for alloys indicated below.

$^b$Asymmetry is calculated using the width of the low temperature side divided by the width of the high temperature side taken at half the peak maximum.

$^c$Peak width is calculated as the actual width of the internal friction peak at half the peak maximum divided by the width if the peak were a Debye peak.

$^d$Sample measurements made after electropolishing. Sample diameter after electropolishing was 0.75 mm.

$^e$Sample measurements made after extraction of 0.45 H sample. Sample diameter was 0.75 mm.
Fig. 3.8. Normalized $Q^{-1}$ versus $1/T$ for the Nb-0.25 O alloy prior to charging, charged with 0.65 hydrogen and with the hydrogen extracted. The background has been subtracted from the data. The disagreement with the theoretical curve at high temperature is probably due to nitrogen contamination.
The 0.65% hydrogen alloy showed a higher peak height resulting from some oxygen contamination. The sample was electropolished from an initial diameter of 1.01 mm to a final diameter of 0.76 mm and the internal friction remeasured. Afterwards, the sample was heated to 873 K and held for one hour under vacuum to extract the hydrogen. The resulting H and τ\textsubscript{0} values are given in Table III. Note that all are within an acceptable range. Fig. 3.8 contains normalized internal friction versus T\textsuperscript{-1} for the Nb+0.2%O sample without hydrogen, with 0.65% hydrogen and with 0.65% hydrogen extracted. The hydrogen concentration does not appear to affect peak shape as was also the case in the vanadium series. From these results it appears that hydrogen does not affect the oxygen relaxation in niobium. A comparison of these results with those from the literature gives favorable results as discussed in 3.4.

3.4. Discussion

The use of internal friction to study interstitials in refractory alloys has found renewed interest in recent years (8-20). Controversy has arisen concerning the occurrence of "clustering" versus "anticlustering" with increasing oxygen concentration (5-12,16-18). The clustering model proposes formation of oxygen pairs and other oxygen clusters while anticlustering proposes a long range repulsive interaction between the oxygen interstitials or between oxygen and other heavy interstitials such as nitrogen. However, the present study is concerned with the possible interaction between hydrogen and oxygen.
The effect of oxygen on the hydrogen relaxation has been examined in the refractory metals (22-25) in the temperature range of 4 to 100 K. Schiller et al. (22) reported that the hydrogen peak height in niobium is dependent on the oxygen concentration. However to the present author's knowledge, the effect of hydrogen on the oxygen peak was not explored previously. The present study investigates the effect of hydrogen on the oxygen Snoek peak.

From the results presented in Table I for V-0-H and Table III for Nb-0-H, it is evident that hydrogen concentration has no systematic effect on peak height or peak shape. It is also evident that hydrogen has no effect on the relaxation parameters, H or $\tau_0$. A comparison of these results with data from the literature supports these assumptions. Table IV compares data from this investigation with literature values.

Weller (12) quotes a value of 1.29 eV for H which is higher than 1.16 eV found for the V-0-H alloys. Note this value is taken from a compilation of internal friction, elastic aftereffect and diffusion measurements. When the values found from the V-0-H internal friction measurements are compared to the internal friction measurements of Boratto et al. (13) agreement is quite acceptable. Boratto et al. (13) found an average H of 1.18 eV and an average $\tau_0$ of $18 \times 10^{-15}$ sec which agrees excellently with the results shown in Table I. Note that Boratto et al. (13) measured V-0 alloys while this investigation included the addition of hydrogen. This indicates that addition of hydrogen has no effect on the vanadium-oxygen peak shape or relaxation parameters.
TABLE IV. Average values for $H$ and $\tau_0$ for the oxygen Snoek peaks, as obtained from Table I and II, compared with literature values

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Experimental Averages</th>
<th>Frequency Measurements</th>
<th>Literature Values</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$H$ (eV)</td>
<td>$\tau_0 \times 10^{15}$ (sec)</td>
<td>$H$ (eV)</td>
</tr>
<tr>
<td>V-0</td>
<td>1.16±0.03</td>
<td>avg: 27</td>
<td>1.14±0.04</td>
</tr>
<tr>
<td></td>
<td>range: 10-40</td>
<td></td>
<td>range: 10-120</td>
</tr>
<tr>
<td>Nb-0</td>
<td>1.12±0.03</td>
<td>avg: .7</td>
<td>1.13±0.10</td>
</tr>
<tr>
<td></td>
<td>range: 3-15</td>
<td></td>
<td>range: 0.2-70</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
A comparison of the Nb-O-H data with Nb-O data in the literature shows excellent agreement as shown in Table IV. The value of 1.12 (±0.03) eV agrees with the value found by Weller et al. (9) who also used internal friction measurements. The value of 7 x 10^{-15} sec also agrees with the ν₀ values found by Weller et al. (9). This indicates that hydrogen has no effect on the oxygen relaxation in niobium.

3.5. Conclusions

1. Internal friction data that undergo a single relaxation can be successfully analyzed using the linear regression procedure discussed in 3.1. The activation parameters that result from this analysis are reliable and agree with others found in the literature. A comparison of the linear regression procedure with a standard frequency analysis showed reasonable agreement.

2. The activation energy for the oxygen Snoek peak in vanadium is 1.16 eV. This value is not affected by hydrogen concentration or oxygen concentration. Hydrogen to oxygen ratios of 0.5, 1.0 and 2.0 were examined and no correlation between hydrogen concentration and activation energy was found. Oxygen concentrations of 0.2% O and 0.5% O were examined and activation energies were the same within experimental error.
3. The pre-exponential factor, $\tau_0$, found for the vanadium-oxygen peak was $27 \times 10^{-15}$ sec. This value is in the same range as that found by Boratto et al. (13) using internal friction.

4. Results for the oxygen Snoek peak in the niobium alloy resulted in an activation energy of 1.12 eV. This agrees with values found in the literature. Variation of the hydrogen to oxygen ratios of 0.5, 1.0 and 2.0 caused no systematic change in H.

5. The pre-exponential factor for the niobium oxygen Snoek peak was $7 \times 10^{-15}$ sec. This agrees with the value of Weller et al. (9) of $7.6 \times 10^{-15}$ sec.
4. INTERNAL FRICTION SPECTRA OF VANADIUM-NIOBIUM ALLOYS WITH HYDROGEN, DEUTERIUM AND HYDROGEN-OXYGEN

4.1. Introduction

Retention of mechanical strength at high temperature as well as resistance to radiation damage suggest that refractory metals are prime candidates for first wall materials in thermonuclear reactors. However, it is known that the presence of hydrogen causes embrittlement in refractory metals (26). It is hoped that internal friction studies of solid solution hydrogen in refractory alloys will provide a better understanding of hydrogen interaction with the substitutional elements as well as with the matrix. The goal of the present research is to determine the activation parameters for hydrogen and deuterium in vanadium-niobium alloys. In addition, the effect of oxygen on the hydrogen internal friction spectrum is examined.

Internal friction spectra of hydrogen in refractory metals has been measured by many researchers. However, the previous studies have predominantly involved hydrogen in the pure metal (22-25, 27-35). Because the hydrogen terminal solubility increases with alloy additions (3), recent interest has been in refractory alloys (36-39). The present research is restricted to the vanadium-rich end of the vanadium-niobium system. Analysis techniques, sample preparation and results are discussed below.
4.2. Experimental Details and Data Analysis Procedures

4.2.1. Sample preparation

Appropriate amounts of vanadium and niobium were weighed to produce the desired compositions of each of the base alloys used in this investigation with final results of the chemical analysis listed in Table VI. The material was then arc zone melted into finger shapes. The fingers which were jacketed in stainless steel to prevent interstitial contamination were hot swaged to 5 mm diameter rods. The 5 mm rods were titanium purified (40) followed by swaging to a final diameter of 1 mm. Wire specimens with lengths of 75 mm and diameters of 1 mm were annealed at 1373 K for 1 hour to relieve cold work prior to gas charging. This results in a grain size of approximately 30 microns for all four V/Nb ratios.

Hydrogen charging of the wires was accomplished through thermal decomposition of uranium hydride as discussed in 3.2.1. A series of 70V30Nb samples was also charged with deuterium using a standard Sieverts type apparatus. The samples were heated to 1273 K under dynamic vacuum of 10^-7 torr. The chamber was then cooled to 1123 K and isolated from the pumping system. Deuterium gas of 99.5 purity was admitted at predetermined pressures. The closed system was held at 1123 K for 2 1/2 hours followed by furnace cooling. An additional series of 70V30Nb samples was charged with oxygen using the procedure described in 3.2.1.

All internal friction measurements were made using the vibrating reed discussed in Chapter 2.
4.2.2. Use of nonlinear regression procedures in data analysis

The primary goal of internal friction is to determine the relaxation time, $\tau$, which leads to the diffusivity of the mobile atom. However, it is often difficult to analyze internal friction spectra because $\tau$ may be represented by some distribution function rather than a unique value. Since it was known from prior experiments (20, 36-37) that for the vanadium-niobium alloys charged with hydrogen, the internal friction spectrum is given by a distribution of relaxation times, use of single relaxation analysis procedures would not be applicable. A distribution of $\tau$ is characterized by an internal friction peak that is wider than the Debye peak (1). Fig. 4.1 compares the Debye peak for the 70V30Nb + 0.55% H alloy with the actual data. Note that the experimental peak is approximately three times broader than the Debye peak. For this reason, Direct Spectrum Analysis (DSA), a nonlinear regression procedure (42-44) developed by J.R. Cost (41) as described in the following was applied to the results of this investigation.

DSA is one of many computer techniques used to analyze internal friction data (12-14,41-44). The primary advantage of DSA is that prior assumptions concerning the form of the spectra are not necessary (42). DSA involves making a sum approximation of the governing integral equation and then using a nonlinear regression least squares technique to unfold the integral equation.
Fig. 4.1. Comparison of the 70V30Nb + 0.55 hydrogen internal friction peak to the theoretical Debye peak calculated for an activation energy of 0.188 eV.
For the case of internal friction versus temperature the governing equation is as follows:

\[ Q^{-1}(T) = \Sigma \Delta_i \frac{\omega \tau_i}{1+(\omega \tau_i)^2} \]  

(4.2.1.)

where \( \Delta_i \) is the relaxation strength of the \( i \)th bin

\( \omega \) is the frequency in rad/sec

\( \tau_i \) is the relaxation time of the \( i \)th bin which is given by the Arrhenius relation as discussed in 3.1.

Because the relaxation time, \( \tau \), is a function of both the pre-exponential factor, \( \tau_0 \), and the activation energy, \( H \), as given by equation 3.1.1., a distribution of \( \tau \) can be caused by either a distribution of \( \tau_0 \) or a distribution of \( H \) or both. In order to solve the integral equation, one must assume that only one variable changes. The present work assumed that \( \tau_0 \) was constant and \( H \) varied.

Based on suggestions by Golub (47) the nonlinear regression technique uses the Levenburg, Marquardt, Morrison algorithm (45-46). Because many iterations are necessary, a FORTRAN program was adapted to analyze the internal friction results.

The regression procedure involves minimizing the difference between the calculated relaxation strength for a given hydrogen concentration and the experimental relaxation strength over a range of temperature and at different activation energies. Upper and lower limits are chosen for \( \tau \) and an estimate is made for \( \tau_0 \). With this input, the activation energy distribution is divided into bins that have a magnitude proportional to the relaxation strength of that bin. The width of the bin is determined by the number of bins
chosen. To begin the iteration procedure, the relaxation strength in all bins is set equal to $\Delta/n$ where $\Delta$ is approximated as twice the peak height, $Q^{-1}_{\text{max}}$, and $n$ is the number of bins chosen by the user. The nonlinear least squares procedure is now used to minimize the difference between the calculated and experimental $\Delta$. The program runs until a given number of iterations is completed or until a given tolerance is reached. The results of the analysis applied to the internal friction data are given as magnitude versus activation energy and are discussed in 4.3.

The disadvantage in using DSA is that $\tau_0$ must be estimated. For the DSA results in this investigation $\tau_0$ values were estimated using two measuring frequencies of approximately 250 and 1500 Hz. This was done for at least one hydrogen or deuterium concentration in each alloy composition. The $\tau_0$ value calculated from the frequency shift was then used in DSA for the other hydrogen or deuterium concentrations measured. In addition $\tau_0$ was also determined at two different hydrogen concentrations in the 70V30Nb alloy as listed in Table V. Note that these agree within the accuracy of these measurements. Therefore the use of $\tau_0$ determined at one hydrogen concentration for other hydrogen concentrations is valid in the DSA analysis. The calculated $\tau_0$ values are listed in Table V below along with other $\tau_0$ values from the literature. Note the agreement between the $\tau_0$ values found in this investigation and those found in the diffusion measurements (48).
Table V. Comparison of $\tau_0$ values found in this investigation with values found in the literature

<table>
<thead>
<tr>
<th>Alloy</th>
<th>H(eV)</th>
<th>$\tau_0$ (x $10^{14}$ sec)</th>
<th>Temperature Range(K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>100V</td>
<td>0.04</td>
<td>4.7</td>
<td>230-473&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
<tr>
<td>90V10Nb</td>
<td>0.09</td>
<td>4.0</td>
<td>230-473&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
<tr>
<td>80V20Nb</td>
<td>0.193</td>
<td>3.7</td>
<td>100-120&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td>75V25Nb</td>
<td>0.144</td>
<td>2.1</td>
<td>230-473&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
<tr>
<td>70V30Nb(+0.25H)</td>
<td>0.196</td>
<td>58</td>
<td>100-120&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td>(+0.5 H)</td>
<td>0.188</td>
<td>73</td>
<td>100-120&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td>(+0.2%0 + 0.26H)</td>
<td>0.199</td>
<td>79</td>
<td>100-120&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td>60V40Nb</td>
<td>0.231</td>
<td>7.5</td>
<td>100-120&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td></td>
<td>0.225</td>
<td>9.43</td>
<td>100-120&lt;sup&gt;c&lt;/sup&gt;</td>
</tr>
<tr>
<td>50V50Nb</td>
<td>0.205</td>
<td>44.3</td>
<td>120-130&lt;sup&gt;d&lt;/sup&gt;</td>
</tr>
<tr>
<td></td>
<td>0.217</td>
<td>1.3</td>
<td>230-473&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
<tr>
<td></td>
<td>0.245</td>
<td>6.4</td>
<td>120-130&lt;sup&gt;c&lt;/sup&gt;</td>
</tr>
<tr>
<td>25V75Nb</td>
<td>0.14</td>
<td>200</td>
<td>80&lt;sup&gt;e&lt;/sup&gt;</td>
</tr>
<tr>
<td></td>
<td>0.227</td>
<td>1.1</td>
<td>230-473&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
<tr>
<td></td>
<td>0.246</td>
<td>6.55</td>
<td>130-150&lt;sup&gt;c&lt;/sup&gt;</td>
</tr>
<tr>
<td>90V10Nb</td>
<td>0.170</td>
<td>2.3</td>
<td>230-473&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
<tr>
<td></td>
<td>0.197</td>
<td>8.41</td>
<td>120-140&lt;sup&gt;c&lt;/sup&gt;</td>
</tr>
<tr>
<td>100Nb</td>
<td>0.082</td>
<td>8.0</td>
<td>230-473&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
</tbody>
</table>

<sup>a</sup>These $\tau_0$ values were calculated from $D_0$ values found by Peterson et al. (48). Tetrahedral to tetrahedral jumps by the hydrogen atom were assumed. It was also assumed that the lattice parameter changes linearly with Nb concentration.

<sup>b</sup>These activation parameters were calculated in this investigation using two measuring frequencies. The alloys were charged with approximately 0.5 % hydrogen unless stated otherwise.

<sup>c</sup>These activation parameters were found by Kim (49).

<sup>d</sup>Data from Cost et al. (36).

<sup>e</sup>Data from Owen et al. (20).
4.3. Experimental Results and Discussion

The hydrogen Snoek peak was investigated as a function of V-Nb ratio as well as a function of hydrogen concentration. The V-Nb alloys used in this investigation are listed in Table VI in both atomic and weight percent.

Table VI. Vanadium – Niobium compositions used in this investigation

<table>
<thead>
<tr>
<th>Atomic %</th>
<th>Weight % desired</th>
<th>Weight %&lt;sup&gt;a&lt;/sup&gt; actual</th>
</tr>
</thead>
<tbody>
<tr>
<td>V - Nb</td>
<td>V - Nb</td>
<td>V - Nb</td>
</tr>
<tr>
<td>90 - 10</td>
<td>83.1 - 16.9</td>
<td>81.2 - 17.6</td>
</tr>
<tr>
<td>80 - 20</td>
<td>68.7 - 31.3</td>
<td>66.6 - 33.3</td>
</tr>
<tr>
<td>70 - 30</td>
<td>56.1 - 43.9</td>
<td>54.2 - 45.4</td>
</tr>
<tr>
<td>60 - 40</td>
<td>45.1 - 54.9</td>
<td>43.1 - 56.0</td>
</tr>
</tbody>
</table>

<sup>a</sup>Vanadium concentration was determined by a titration procedure while niobium concentration was determined by flame emission.

The various hydrogen concentrations are listed in Table VII with results of the measurements discussed in subsequent sections.
Table VII. Interstitial concentrations used in this investigation

<table>
<thead>
<tr>
<th>V - Nb ratio</th>
<th>Atomic % H</th>
<th>Atomic % O</th>
<th>Atomic % D</th>
</tr>
</thead>
<tbody>
<tr>
<td>90 - 10</td>
<td>0.25</td>
<td>residual</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.56</td>
<td>&quot;</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1.94</td>
<td>&quot;</td>
<td></td>
</tr>
<tr>
<td>80 - 20</td>
<td>0.08</td>
<td>residual</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.23</td>
<td>&quot;</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.60</td>
<td>&quot;</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.94</td>
<td>&quot;</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2.4</td>
<td>&quot;</td>
<td></td>
</tr>
<tr>
<td></td>
<td>4.0</td>
<td>&quot;</td>
<td></td>
</tr>
<tr>
<td>70 - 30</td>
<td>0.25</td>
<td>residual</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.55</td>
<td>&quot;</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1.06</td>
<td>&quot;</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1.78</td>
<td>&quot;</td>
<td></td>
</tr>
<tr>
<td>70 - 30</td>
<td>residual</td>
<td>residual</td>
<td>0.18</td>
</tr>
<tr>
<td></td>
<td>&quot;</td>
<td>&quot;</td>
<td>0.29</td>
</tr>
<tr>
<td></td>
<td>&quot;</td>
<td>&quot;</td>
<td>0.32</td>
</tr>
<tr>
<td></td>
<td>&quot;</td>
<td>&quot;</td>
<td>0.51</td>
</tr>
<tr>
<td>70 - 30</td>
<td>0.26</td>
<td>0.2</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.49</td>
<td>0.2</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.76</td>
<td>0.2</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1.3</td>
<td>0.2</td>
<td></td>
</tr>
<tr>
<td>60 - 40</td>
<td>0.11</td>
<td>residual</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.51</td>
<td>&quot;</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.91</td>
<td>&quot;</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2.1</td>
<td>&quot;</td>
<td></td>
</tr>
</tbody>
</table>
4.3.1. Hydrogen Snoek peak in V–Nb alloys

Internal friction due to the presence of hydrogen was measured for each of the V–Nb ratios listed in Tables VI and VII. Hydride precipitation was found in the 90V10Nb and 80V20Nb alloys. The hydrogen Snoek peak was found in the 60V40Nb, 70V30Nb and 80V20Nb alloys. Note that evidence of both a hydride peak and Snoek peak was found in the 80V20Nb alloy as will be discussed in 4.3.4. Only the hydrogen peak will be discussed here.

Results of the 70V30Nb and 60V40Nb alloys at various hydrogen concentrations are shown in Fig. 4.2 and Fig. 4.3 respectively. The results have been adjusted with respect to frequency which will shift the curve with respect to temperature. Other than a slight temperature shift, the points shown are actual data points. Fig. 4.4 shows the hydrogen concentration versus peak height for the various alloys measured in this investigation. Note the linear increase in peak height with increasing hydrogen concentration as is characteristic of a Snoek type relaxation. From this graph, it is evident that for nonhydride forming V-Nb alloys, the peak height depends only on hydrogen concentration and not on V/Nb ratio. For hydrogen concentrations greater than approximately one atomic percent in the 80V20Nb alloy, hydride precipitation was found as discussed in section 4.3.5.

In addition to an increasing peak height with increasing hydrogen concentration, the peak temperature also shifts to lower temperature as shown in Fig. 4.5. This trend was also observed by
Fig. 4.2. Experimental data for the 70V30Nb alloy at various hydrogen concentration. All results have been corrected to a frequency of 270 Hz.
Fig. 4.3. Experimental data for the 60V40Nb alloy at various hydrogen concentration. All results have been corrected to a frequency of 270 Hz.
Fig. 4.4. Hydrogen concentration versus peak height for the V/Nb ratios listed.
Fig. 4.5. Maximum temperature versus hydrogen concentration for the V/Nb ratios listed.
Owen et al. (20) in V-Nb alloys and by Cannelli et al. (38,39) in Nb-Ti alloys. Cannelli et al. (38) propose that the temperature shift found in Nb-Ti alloys results from the existence of titanium-hydrogen complexes such as Ti-H, Ti-H₂, Ti-H₃... with the higher order complexes having lower activation energies. As hydrogen concentration is increased, the number of higher-order complexes increases and the overall activation energy decreases which results in a shift of the internal friction peak to lower temperatures.

The shift to lower temperature with increasing hydrogen concentration in the V-Nb alloys in this investigation indicates that the activation energy also should decrease with increasing hydrogen concentration. To determine the effect of hydrogen concentration on activation energy, Direct Spectrum Analysis (DSA), as discussed in section 4.2.2. was performed on each of the internal friction results. Results of DSA for each of the nonhydride forming alloys is listed in Table VIII. The activation energies listed were chosen as the average value from the activation energy distribution results. \( \tau_0 \) values chosen to be used in DSA are also listed in the Table VIII. Note the \( \tau_0 \) values were calculated from frequency shift measurements using the frequencies and temperatures listed. The activation energy calculated from the frequency shift is also listed.
Table VIII. Activation energies as determined from DSA for the 60V40Nb and 70V30Nb alloys

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Interstitial Concentration</th>
<th>H(eV)</th>
<th>T(K)</th>
<th>f(Hz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>60V40Nb</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(\tau_0 = 7.5 \times 10^{-14} ) sec</td>
<td>0.11 H</td>
<td>0.244</td>
<td>121.96</td>
<td>251.1a</td>
</tr>
<tr>
<td></td>
<td>0.51 H</td>
<td>0.229</td>
<td>117.00</td>
<td>219.6a</td>
</tr>
<tr>
<td></td>
<td>0.91 H</td>
<td>0.225</td>
<td>112.73</td>
<td>242.6a</td>
</tr>
<tr>
<td></td>
<td>2.1 H</td>
<td>0.212</td>
<td>108.83</td>
<td>255.9a</td>
</tr>
<tr>
<td>(\tau_0 = 7.5 \times 10^{-14} ) sec</td>
<td>0.51 H</td>
<td>0.231</td>
<td>117.00</td>
<td>219.6b</td>
</tr>
<tr>
<td>70V30Nb</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(\tau_0 = 5.8 \times 10^{-13} ) sec</td>
<td>0.25 H</td>
<td>0.196</td>
<td>110.00</td>
<td>270.87</td>
</tr>
<tr>
<td></td>
<td>0.55 H</td>
<td>0.194</td>
<td>105.3</td>
<td>236.4a</td>
</tr>
<tr>
<td></td>
<td>1.06 H</td>
<td>0.180</td>
<td>102.26</td>
<td>214.1a</td>
</tr>
<tr>
<td></td>
<td>1.78 H</td>
<td>0.173</td>
<td>99.43</td>
<td>258.96a</td>
</tr>
<tr>
<td>(\tau_0 = 5.8 \times 10^{-13} ) sec</td>
<td>0.25 H</td>
<td>0.196</td>
<td>110.00</td>
<td>270.7b</td>
</tr>
<tr>
<td>(\tau_0 = 7.3 \times 10^{-13} ) sec</td>
<td>0.55 H</td>
<td>0.188</td>
<td>105.9</td>
<td>236.5</td>
</tr>
</tbody>
</table>

\(a\) Determined from DSA using the \(\tau_0\) listed.

\(b\) Activation energy and \(\tau_0\) determined from the frequency and temperature results listed.

Fig. 4.6 shows the distributions for various hydrogen concentrations in the 70V30Nb alloy. Results for the 60V40Nb are shown in Fig. 4.7. This is plotted as spectral amplitude which may be thought of as a probability versus activation energy. The curve
Fig. 4.6. DSA results for the 70V30Nb alloy. Envelopes are generated using Gaussian distribution function.
Fig. 4.7. DSA results for the 60V40NB alloy. Envelopes are generated using Gaussian distribution function.
drawn through the bar graph is generated using a Gaussian
distribution function proposed by Kirchheim (53) and is discussed
later in this thesis. The Gaussian function has been normalized
with respect to the DSA results. Note the excellent agreement
between the DSA results and the Gaussian function. Also listed with
the results is the average activation energy as determined by DSA
and $\sigma$, a measure of the width of the distribution. Note that $\sigma$ does
not vary much with hydrogen concentration.

A comparison of activation energies found in this investigation
to those found by diffusion measurements (48) is shown in Fig. 4.8. Also shown are activation energies found by Kim (49) for the niobium
rich alloys. Note that while consistently larger values of $H$ were
found for the internal friction measurements compared to the
diffusion measurements, there is considerable uncertainty in the
internal friction values. This is the result of uncertainty in
determining the exact peak temperature for the internal friction
measurements. Because the internal friction peaks are so broad, as
was seen in Fig. 4.1, it is difficult to choose the peak temperature
and consequently difficult to determine $H$ to better accuracy. The
primary consideration is that the trends found in diffusion
measurements made in the temperature range of 230 to 473 K are
repeated by the internal friction measurements made at 100 to 120 K.

Because the activation energies found by internal friction were
consistently larger than those found by diffusion, it is possible
that the hydrogen is being trapped by the substitutional atoms at
the lower temperatures. Verification of this assumption is not
Fig. 4.8. Comparison of activation energy found by internal friction to that found by diffusion measurements.
possible at this time. Measurements of the Gorsky effect in these alloys would possibly clarify if trapping occurs. Trapping can be assumed if the activation energy is found to increase at the lower temperatures at which Gorsky effect would be measured.

A comparison of the activation energy versus hydrogen concentration is given in Fig. 4.9. Note that the activation energy decreases with increasing hydrogen concentration as would be predicted from the decrease in peak temperature with increasing hydrogen concentration. This trend was also observed in refractory alloys by Owen (20), Snead et al. (37) and Cannelli (38,39) as discussed previously. In addition this trend has been found in amorphous metals discussed later.

The hydrogen Snoek effect in 50V50Nb has been examined by Snead et al. (37) with similar results to those found in this investigation. Snead et al. (37) investigated hydrogen concentrations from 2.5 to 28 atomic percent in the temperature range of 6 to 320 K and frequencies of 500 to 5000 Hz. Using data taken at different frequencies, Snead et al. (37) were able to determine the activation energy using the peak shift method which yielded values of 0.21 and 0.19 eV for hydrogen concentrations of 8 and 28 % respectively. This agrees with the value given by Peterson et al. (48) of 0.21 eV. Snead et al. (37) also used the linear regression method of Weller (9,10) discussed in 3.2 to analyze their results. Because this analysis assumes a single relaxation process the results are somewhat inconsistent. The low temperature side of the peak gave a value of 0.05 eV and $\tau_0$ of approximately $10^{-8}$ sec
Fig. 4.9. Activation energy found using DSA versus hydrogen concentration for the V-Nb alloys listed.
while the high temperature side yields values of 0.25 eV and $\tau_0$ of $10^{-13}$ sec. Use of the Weller analysis on the data in this investigation yields similar results. Snead et al. (37) conclude that the activation energy for H in the 50V50Nb alloy is best represented by a Gaussian distribution ranging from 0.05 to 0.25 eV centered at 0.21. Use of DSA confirms this assumption (36).

Comparison of the results in Fig. 4.6 and Fig. 4.7 to those of Cost (36) for the 50V50Nb alloy reveal the same type of distribution as for the 70V30Nb and 60V40Nb alloys. The distribution of activation energies and relaxation times is assumed to result from various chemical environments available to the hydrogen atoms. Because near neighbor and next near neighbor influences are probable there are many "types" of sites the hydrogen may see. The actual peak is approximately 3 times as broad as a singly activated Debye peak as seen in Fig. 4.1 which seems to support this idea.

In conclusion there are several points to be considered for the hydrogen Snoek peak in the nonhydride forming V-Nb alloys.

1. The peak height increases linearly with hydrogen concentration. Therefore V/Nb ratio does not appear to change the relaxation strength.

2. The peak shifts to higher temperature as the niobium concentration increases for a constant hydrogen concentration. This indicates the activation energy increases with niobium content for the vanadium-rich alloys. Analysis of the frequency shift of the hydrogen peak in these alloys verifies this result.
3. For a given alloy composition, the peak shifts to lower temperatures with increasing hydrogen concentration which indicates a decreasing activation energy. DSA confirmed this assumption.

4. The internal friction peaks were broader than a single relaxation peak which indicates a distribution of activation energies. DSA confirmed that a Gaussian distribution of activation energies exists for the nonhydride forming alloys. The Gaussian function proposed by Kirchheim et al. (53) to explain the hydrogen data in amorphous alloys is found to fit the DSA results excellently.

5. A comparison of activation energies found by internal friction to those found by diffusion measurements shows considerable agreement. The internal friction results were consistently higher by approximately 0.02 eV. Because internal friction was measured at 100 to 120 K and the diffusion measurements were made at 230 to 473 K, it is possible the difference is the result of trapping of the hydrogen by substitutional atoms at the lower temperature. Verification of this assumption would require additional measurements at even lower temperatures as is possible using Gorsky measurements.
4.3.2. Comparison of hydrogen effects in V-Nb alloys and amorphous metals

Internal friction has also been used to study hydrogen in solid solution in many amorphous metals (50-60). Of particular interest is the work of Stolz et al. (55) and Kirchheim (54) because of the similarities between their findings and the results of this investigation. Hydrogen dissolved in various amorphous alloys shows a broad asymmetric internal friction peak which shifts toward lower temperatures with increasing hydrogen concentration (52,55). This indicates that a shift in activation energy may also occur as was found here for the V-Nb alloys. As in the V-Nb alloys the peak was found to be much broader than a Debye peak. Results of the Pd-Si alloy indicate that over the temperature range measured by Kirchheim et al. (53) the diffusivity increased with increasing hydrogen concentration while the activation energy decreased. Note that DSA indicates such a decrease in activation energy with increasing hydrogen concentration for the V-Nb alloys as well. For most amorphous metals the peak height shows a linear increase with hydrogen concentration as was found in the V-Nb alloys. However this was not the case for the amorphous Ni$_{35}$Ti$_{65}$ alloy as will be discussed later.
For hydrogen in a pure crystalline metal, the activation energy should not depend on concentration unless hydrogen clustering occurs. All sites are equivalent, therefore the energy required for hydrogen to move is not affected by the amount of hydrogen present. However in the V-Nb alloys not all sites are equivalent. There are many combinations of near neighbor and next near neighbor environments possible because of the presence of both V and Nb. Therefore some combinations may have lower activation energies than others which leads to the activation energy distribution found for these alloys. Kirchheim et al. (53) already proposed that in amorphous metals there is such a spectrum of sites which have associated with them different values for the relaxation energy.

Hydrogen in amorphous metals is proposed to occupy sites which are similar to the interstitial sites in crystalline metals. In both amorphous metals and V-Nb alloys, a Gaussian distribution of activation energies is found. Kirchheim et al. (53) describe the Gaussian distribution for amorphous metals using Fermi-Dirac statistics as discussed below. The spectrum of energies is assumed to be continuous with a density of sites, \( n \), given by the following Gaussian function

\[
 n(G) = \frac{dN}{dG} = \frac{1}{\sqrt{\pi} \alpha} \exp[\left(-\frac{G - G_0}{\sigma}\right)^2] \quad (4.3.1.)
\]

where \( dN \) is the number of sites available for hydrogen at energy \( G \) within the interval \( dG \)

\( G_0 \) is the mean energy

\( \sigma \) is the width of the Gaussian function
The envelopes in Fig. 4.6 and Fig. 4.7 were generated using this equation.

The values for $G_0$ and $\sigma$ were found through statistical analysis of the DSA results. Values found for the V-Nb alloys are compared to results found for amorphous metals (53) in Table IX. The results for the amorphous metals were determined experimentally from electrochemical measurements. The $G_0$ values determined by Kirchheim et al. (53) are the mean free enthalpy of solution values with respect to the standard state, while the values found in this investigation are activation energies. While comparison of the $G_0$ values in the two cases seems not to be valid, a comparison of $\sigma$ leads to interesting conclusions. For a crystalline material where all sites have equivalent energy, $\sigma$ equals zero. Since $\sigma$ is greater than zero, the V-Nb alloys must contain sites of varying energy or be noncrystalline. Since the later is not the case, the alloy must have a distribution of energies as predicted by DSA. Note that $\sigma$ for the V-Nb alloys is lower than for the as-quenched amorphous metals. This would indicate the energy distribution for the amorphous metals is broader than in the V-Nb alloys. Noteworthy is the effect of annealing on the $\sigma$ for the Pd-Cu-Si alloy. As annealing temperature increases, $\sigma$ decreases indicating the structure is moving from amorphous to crystalline.
Table IX. Comparison of $\sigma$ for the V-Nb alloys in this investigation to $\sigma$ for the amorphous metals

<table>
<thead>
<tr>
<th>Alloy</th>
<th>$G_0$(eV)</th>
<th>$\sigma$(eV)</th>
<th>Temperature(K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>80V20Nb</td>
<td>0.178</td>
<td>0.119</td>
<td>91.7$^a$</td>
</tr>
<tr>
<td>70V30Nb</td>
<td>0.180</td>
<td>0.102</td>
<td>102.3$^a$</td>
</tr>
<tr>
<td>60V40Nb</td>
<td>0.225</td>
<td>0.118</td>
<td>112.7$^a$</td>
</tr>
<tr>
<td>77.5Pd6Cu16.5Si</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>as-quenched</td>
<td>0.233</td>
<td>0.151</td>
<td>345$^b$</td>
</tr>
<tr>
<td>annealed 30 min. at 490K</td>
<td>0.233</td>
<td>0.146</td>
<td>345$^b$</td>
</tr>
<tr>
<td>annealed 30 min. at 680K</td>
<td>0.149</td>
<td>0.097</td>
<td>345$^b$</td>
</tr>
<tr>
<td>annealed 30 min. at 875K</td>
<td>0.222</td>
<td>0.134</td>
<td>345$^b$</td>
</tr>
<tr>
<td>50Ni32Pd18P</td>
<td>0.35</td>
<td>0.168</td>
<td>345$^{b,c}$</td>
</tr>
<tr>
<td>64Ni36Zr</td>
<td>0.025</td>
<td>0.181</td>
<td>333$^{b,c}$</td>
</tr>
<tr>
<td>62Ni29Ti19Zr</td>
<td>0.181</td>
<td>0.161</td>
<td>452$^{b,c}$</td>
</tr>
</tbody>
</table>

$^a$Measured in this investigation containing approximately 1% hydrogen.

$^b$ From Kirchheim et al. (53).

$^c$ Measurements made on the as-quenched alloy.

Kirchheim et al. (53) and Stolz (52) make use of Fermi-Dirac statistics in evaluating the Gaussian energy distribution given by equation 4.3.1. From this, Stolz (52) proposes that only hydrogen at the hydrogen Fermi level contributes to the relaxation.

The Fermi level of hydrogen is similar to the Fermi energy for electrons in metals. The Fermi energy for the electrons is defined
as the energy of the highest filled level when the metal is at the ground state (66). The ground state occurs when the system is at absolute zero. At the ground state, only energy levels below the Fermi energy are occupied. As the temperature increases above 0 K, the kinetic energy of the electrons allows some electrons to move into higher levels leaving some of the lower orbitals vacant. The probability that an energy level is occupied is given by the Fermi-Dirac distribution function:

\[
P(\varepsilon) = \frac{1}{\exp\left(\frac{\varepsilon - \mu}{kT}\right) + 1} \tag{4.3.2.}\]

where \(\varepsilon\) is the energy of a given orbital

\(\mu\) is the chemical potential which is equal to the Fermi energy at absolute zero.

In addition, the Fermi energy for electrons in metals is proportional to the number of electrons present (66).

Application of Fermi-Dirac statistics to the Gaussian energy distribution, \(n(G)\), found for hydrogen in amorphous alloys results in the following occupancy function:

\[
o(G) = \frac{n(G)}{\exp\left(\frac{G - \mu}{kT}\right) + 1} \tag{4.3.3.}\]

where \(o(G)\) is the occupancy distribution

\(\mu\) is the Fermi energy of hydrogen or its chemical potential

Each energy, \(G\), will have associated with it a limited number of sites given by \(n(G)\) where the probability that these sites are occupied is given by \(o(G)\). Integration of equation 4.3.3. leads to
the following relationship between the concentration and $\mu$:

$$2c = 1 \pm \text{erf}(\frac{G_0 - \mu}{\sigma}) \quad (4.3.4.)$$

As in the case of electrons, the lowest energy states will be filled first and the Fermi energy of the hydrogen is proportional to the total number of hydrogen atoms present.

From this Stolz (52) proposes that the relaxation is determined by the density of sites at the Fermi level of hydrogen, i.e., only hydrogen at the Fermi level contributes to the relaxation. As the hydrogen concentration increases the Fermi energy level increases as does the internal friction peak height. Therefore the peak height is proportional to the hydrogen Fermi energy. In addition to an increase in peak height, a shift of the peak to lower temperatures with increasing hydrogen concentration is also found experimentally as seen in Fig. 4.2. This is presumed to be the result of filling the lower energy sites. As more hydrogen is added, higher energy sites are filled and the overall activation energy decreases shifting the peak to lower temperatures. Similar results have been found in internal friction measurements of amorphous metals (50,55).

Stolz et al. (55) measured the internal friction spectra for Ni$_{35}$Ti$_{65}$ with varying amounts of hydrogen. The peak was found to increase as well as to shift to lower temperature with increasing hydrogen concentration from 0.02 to 0.1 % H. However increasing the hydrogen concentration further resulted in a decrease of the peak. This is explained by the following. In amorphous metals, there is a distribution of site energies unlike in a perfect crystal were all sites are equivalent. Application of stress to the crystalline material results in reorientation of the interstitials giving rise
to anelastic relaxation where the relaxation strength is proportional to the total concentration of interstitial atoms. However, in the amorphous metals and nonperfect crystalline metals such as V-Nb alloys, the width of the distribution of site energies already present is larger than the energy change caused by the applied stress. Upon application of stress, only atoms around the Fermi level of hydrogen will be affected and contribute to the internal friction peak. The effective concentration, $c_{eff}$ is given by

$$c_{eff} = n(\mu)kT \quad (4.3.5.)$$

where $\mu$ is the Fermi level of hydrogen and $n(\mu)$ is the density of sites at the Fermi level. Stolz (55) proposes that the decrease in relaxation strength in the Ni$_{35}$Ti$_{65}$ alloy at a hydrogen concentration of 0.15 is the result of several well separated maxima which can be attributed to different types of sites. He proposes that tetrahedral sites with four Ti atoms are filled first. As more hydrogen is added 3Ti-1Ni sites will begin to be filled and the relaxation strength will further increase. Unfortunately, this could not be verified for the V-Nb alloys experimental reasons. It would be of interest to see if further increases in hydrogen concentration in the V-Nb alloys result in a decrease in peak height.

In conclusion there are several useful comparisons to consider between the hydrogen Snoek peak in the nonhydride forming V-Nb alloys and results found in amorphous metals.
1. The internal friction peaks in the V-Nb alloys were broader than a single relaxation peak which indicates a distribution of activation energies. DSA confirmed that a Gaussian distribution of activation energies exists for the nonhydride forming alloys. The Gaussian function proposed by Kirchheim et al. (53) to explain the hydrogen data in amorphous alloys is found to fit the DSA results excellently.

2. Internal friction of amorphous metals charged with various amounts of hydrogen also reveal peaks broader than Debye peaks that shift to lower temperatures with increasing hydrogen. The energy distributions are found to be Gaussian for the amorphous metals and for the V-Nb alloys. Kirchheim et al. (53) propose that only the hydrogen atoms at the Fermi level of hydrogen contribute to the relaxation in amorphous metals. Here it is proposed that this may be true for the V-Nb alloys as well. To verify this assumption may require additional measurements at higher hydrogen concentrations.

3. Comparison of $\sigma$, the width of the Gaussian distribution, reveals a broader distribution for the amorphous metals than for the crystalline V-Nb alloys as would be expected. $\sigma$ was not found to vary with hydrogen concentration or with V/Nb ratio in the V-Nb alloys.
4.3.3. **Deuterium Snoek peak in V - Nb alloys**

One objective of this investigation was to compare the internal friction response due to hydrogen to that of deuterium. To accomplish this a set of the titanium purified (40) 70V30Nb samples was charged with various deuterium concentrations and measured in the vibrating reed. Results of the internal friction measurements are shown in Fig. 4.10. Note the peak height increases linearly with deuterium concentration as was found in the hydrogen charged alloys.

Fig. 4.11 compares $Q_{\text{max}}^{-1}$ versus interstitial concentration for the hydrogen and deuterium charged alloys. Note the deuterium has a higher relaxation strength than the hydrogen. This is also evident in Fig. 4.12 which compares internal friction data for the 70V30Nb alloy charged with 0.55 H and 0.51 D. The relaxation strength, $\Delta$, is defined as the following:

$$\Delta = \frac{M_u - M_r}{M_r} \quad (4.3.6.)$$

where $M_u =$ unrelaxed modulus

$M_r =$ relaxed modulus.

Therefore comparison of the modulus effects resulting from addition of hydrogen to the effect of deuterium may clarify this effect. Future elastic constant measurements proposed for this alloy system, may also clarify this effect.

Also evident in Fig. 4.12 is that the deuterium peak is wider than the hydrogen peak as well as shifted to higher temperatures. These trends indicate that the relaxation activation energy is higher for deuterium than hydrogen. To verify this the 70V30Nb +
Fig. 4.10. Internal friction results for the 70V30Nb alloy with various deuterium concentrations. All results corrected to 270 Hz.
Fig. 4.11. Comparison of relaxation strength due to hydrogen and to deuterium in 70V30Nb.
Fig. 4.12. Comparison of internal friction results for 0.51 D to 0.55 H in 70V30Nb. Both are corrected to a frequency of 270 Hz.
0.29% D was measured at two frequencies as shown in Fig. 4.13. Use of the two frequencies allowed determination of H and τ₀. The results are tabulated below along with the diffusion results of Peterson et al. (48).

Table X. Comparison of the activation parameters found by diffusion (48) to those determined in this investigation using internal friction measurements

<table>
<thead>
<tr>
<th>Alloy</th>
<th>H(eV)</th>
<th>τ₀( x 10^{14} sec)</th>
<th>Temperature Range(K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>70V30Nb + 0.25 H</td>
<td>0.196</td>
<td>59</td>
<td>110.0^a</td>
</tr>
<tr>
<td>70V30Nb + 0.29 D</td>
<td>0.229</td>
<td>12</td>
<td>119.4^a</td>
</tr>
<tr>
<td>75V25Nb + H</td>
<td>0.144</td>
<td>2.1</td>
<td>230-473^b</td>
</tr>
<tr>
<td>75V25Nb + D</td>
<td>0.167</td>
<td>2.6</td>
<td>230-473^b</td>
</tr>
</tbody>
</table>

^a Internal friction measurements.

^b Diffusion measurements (48).

Notice that the activation energies for the deuterium are consistently higher than those for the hydrogen. Differences in the magnitude of τ₀ are probably due to inaccuracies in determining the actual peak temperature which leads to error in the τ₀ calculation as discussed in 4.3.1.

The shift of the peak to lower temperature with increasing deuterium concentration is also evident in Fig. 4.10. To determine how this affects the activation energy DSA was used to analyze the
Fig. 4.13. Results of internal friction for 70V30Nb + 0.29% D measured at two frequencies.
internal friction peaks with the results shown in Fig. 4.14. Note the activation energy still exhibits a Gaussian distribution and that the activation energy does decrease with increasing deuterium concentration as shown in Table XI below.

Table XI. DSA results for the 70V30Nb + D alloy

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Interstitial Concentration</th>
<th>H(eV)</th>
<th>T(K)</th>
<th>f(Hz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>70V30Nb</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>( \tau_0 = 1.2 \times 10^{-13} \text{ sec} )</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.18 D</td>
<td>0.228</td>
<td>120.4</td>
<td>272.7(^a)</td>
</tr>
<tr>
<td></td>
<td>0.29 D</td>
<td>0.224</td>
<td>119.4</td>
<td>274.4(^a)</td>
</tr>
<tr>
<td></td>
<td>0.51 D</td>
<td>0.217</td>
<td>119.5</td>
<td>279.6(^a)</td>
</tr>
</tbody>
</table>

\( \tau_0 = 1.2 \times 10^{-13} \text{ sec} \)

|             | 0.29 D                      | 0.229 | 119.4 | 274.4\(^b\) |
|             |                             |       | 130.15| 1724.8       |

\(^a\) Determined from DSA using the \( \tau_0 \) listed.

\(^b\) Activation energy and \( \tau_0 \) determined from the frequency and temperature results listed.

Comparison of the hydrogen Snoek peak to the deuterium peak lead to the following conclusions:

1. While the peak height varies linearly with interstitial concentration for both hydrogen and deuterium, the deuterium has a greater relaxation strength than the hydrogen.
Fig. 4.14. DSA results for the 70V30NB alloy charged with deuterium. Envelopes are generated using Gaussian distribution function.
2. The peak is wider for deuterium than hydrogen and occurs at a higher temperature which indicates a higher activation energy. Analysis of the shift with frequency confirmed a higher activation energy for deuterium than for hydrogen.

3. A shift to lower temperature with increasing deuterium indicates that the activation energy decreases with increasing deuterium. This was confirmed by DSA. DSA also revealed a Gaussian energy distribution as was found for the hydrogen.
4.3.4. **Effect of oxygen on the hydrogen Snoek peak**

Hydrogen in solid solution in metals automatically leads to the question of a possible interaction of hydrogen with other interstitials, in particular oxygen (20, 58-65). This investigation had as its objective to determine if oxygen affects the hydrogen Snoek peak in V-Nb alloys thus indicating an interaction. To meet this objective, a 2.5 mm rod of 70V30Nb was charged with 0.2% oxygen using the technique described in 3.2.1. After homogenization, the rod was swaged to 1 mm and samples of 75 mm in length were cut. The samples were then annealed, charged with hydrogen and measured in the vibrating reed apparatus.

Results of the internal friction measurements are contained in Fig. 4.15. Note the peak height increases linearly with increasing hydrogen concentration as was found in the alloys not containing oxygen. To determine if oxygen affects the relaxation strength in this alloy, $Q^{-1}_{max}$ is plotted versus hydrogen concentration for hydrogen charged 70V30Nb with and without oxygen in Fig. 4.16. Note that oxygen does not affect the relaxation strength in this alloy for the composition range measured. This is also evident in Fig. 4.17 which compares 70V30Nb charged with 0.55% H to 0.2% O + 0.49% H. Note there is a slight difference in peak height but this can be attributed to the difference in hydrogen concentration.

To determine if oxygen has any effect on the peak shape, the 0.55% H and 0.2% O + 0.49% H were normalized with respect to their $Q^{-1}_{max}$ values and corrected to a frequency of 270 Hz. The results are plotted in Fig. 4.18. The oxygen charged peak is shifted to
Fig. 4.15. Results of internal friction for 70V30Nb + 0.2% oxygen at various hydrogen concentrations. All results corrected to 270 Hz.
Fig. 4.16. Comparison of $Q^{-1}_{\text{max}}$ for 70V30Nb charged with and without oxygen at hydrogen concentrations listed.
Fig. 4.17. Results of internal friction for 70V30Nb with and without oxygen charging. Results corrected to 270 Hz.
Fig. 4.18. Results of normalized internal friction for 70V30Nb with and without oxygen charging. Results corrected to 270 Hz.
slightly higher temperatures but this can be attributed to the difference in hydrogen concentration. From this plot it is apparent that oxygen does not effect the shape of the hydrogen Snoek peak.

To determine the possible effect oxygen may have on the activation parameters, the 70V30Nb + 0.2% O + 0.26% H sample was measured at two different frequencies. The $\tau_0$ and H values determined from this frequency analysis are compared to those described earlier for the same alloy not charged with oxygen. This comparison is given in Table XII. Note that oxygen does not change the activation energy or $\tau_0$ of the hydrogen peak within the accuracy of these experiments.

Table XII. Comparison of the activation parameters found for the 70V30Nb samples with and without oxygen through analysis of the temperature shift with frequency

<table>
<thead>
<tr>
<th>Interstitial Concentration</th>
<th>$H$(eV)</th>
<th>$\tau_0$(x $10^{14}$ sec)</th>
<th>T(K)</th>
<th>f(Hz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.2% O + 0.49% H</td>
<td>0.199</td>
<td>79</td>
<td>113.5</td>
<td>276.8</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>125.0</td>
<td>1809.3</td>
</tr>
<tr>
<td>0.25% H</td>
<td>0.196</td>
<td>58</td>
<td>110.0</td>
<td>270.7</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>120.4</td>
<td>1524.9</td>
</tr>
<tr>
<td>0.55%H</td>
<td>0.188</td>
<td>73</td>
<td>105.9</td>
<td>236.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>116.95</td>
<td>1664.1</td>
</tr>
</tbody>
</table>

As a final method to explore the effect of oxygen on the hydrogen Snoek peak, DSA was used to analyze the internal friction results. Results are shown in Fig. 4.19. Note that the activation
Fig. 4.19. DSA results for the 70V30Nb + 0.2% oxygen alloy. Envelopes are generated using Gaussian distribution function.
energy distribution is Gaussian as was found in the sample not containing oxygen. The values found for $\sigma$ also agree quite well indicating that oxygen does not broaden the activation energy spectrum. The average $H$ values are listed in Table XIII below. Comparison of these values to those in Table VIII for samples not charged with oxygen shows that oxygen does not affect the activation energy and $\tau_0$ within the accuracy of these experiments.

Table XIII. Results of DSA and the frequency shift for the 0.2% oxygen charged 70V30Nb alloy at various hydrogen concentrations

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Interstitial Concentration</th>
<th>$H$(eV)</th>
<th>$T$(K)</th>
<th>$f$(Hz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>70V30Nb-0.2 0</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\tau_0 = 7.9 \times 10^{-13}$ sec</td>
<td>0.26 H</td>
<td>0.198</td>
<td>112.90</td>
<td>276.9$^a$</td>
</tr>
<tr>
<td></td>
<td>0.49 H</td>
<td>0.190</td>
<td>109.18</td>
<td>280.1$^a$</td>
</tr>
<tr>
<td></td>
<td>0.76 H</td>
<td>0.187</td>
<td>106.38</td>
<td>268.2$^a$</td>
</tr>
<tr>
<td></td>
<td>1.3 H</td>
<td>0.177</td>
<td>101.94</td>
<td>279.4$^a$</td>
</tr>
<tr>
<td>$\tau_0 = 7.9 \times 10^{-13}$ sec</td>
<td>0.26 H</td>
<td>0.199</td>
<td>113.50</td>
<td>276.8$^b$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>125.0</td>
<td>1809.3</td>
</tr>
</tbody>
</table>

$^a$Determined from DSA using the $\tau_0$ listed.

$^b$Activation energy and $\tau_0$ determined from the frequency and temperature results listed.
The following conclusions can be made from the comparison of the 70V30Nb results with and without oxygen:

1. The peak height is found to increase linearly with hydrogen concentration for both the alloys charged and not charged with oxygen. Oxygen does not affect the relaxation strength of the hydrogen in the 70V30Nb alloy over the range of hydrogen concentrations measured.

2. Oxygen does not affect the shape of the hydrogen Snoek peak which indicates the relaxation parameters also should not be affected.

3. Comparison of activation energies and $\tau_0$ for the alloys charged or not charged with oxygen as determined from frequency shift and DSA reveal that oxygen does not affect the relaxation parameters.

4. DSA results of the oxygen charged samples were essentially the same as those for the samples not charged with oxygen. Oxygen did not affect $\sigma$, the width of the distribution or the shape or the distribution.
4.3.5. Coexistence of hydride and hydrogen in solid solution

As mentioned in 4.3.1., hydride precipitation was found in both the 90V10Nb and 80V20Nb alloys. Results for the 90V10Nb are shown in Fig. 4.20. The hydride peak is similar in shape and in a temperature range comparable to that found in the pure vanadium metal (28,29). To confirm that the peak results from hydride precipitation, low temperature microscopy was performed. On cooling down, precipitation occurred at 232 K which agrees quite well with the high temperature end of the peak for 1.94 % H as shown in Fig. 4.20. A hydrogen Snoek peak was not detected in the 90V10Nb alloy.

Internal friction results for the hydrogen charged 80V20Nb alloy are shown in Fig. 4.21. For clarity only the results for hydrogen concentrations greater than 0.6% are shown. It was found that the hydrogen peak height reaches a maximum at 0.94% H, decreasing with further hydrogen additions. Note the double peak structure found at the 4.01% composition. The low temperature peak is due to hydrogen in solid solution while the high temperature peak is the result of hydride precipitation as was the case in the 90V10Nb alloy. Low temperature microscopy was performed on the 0.94%, 2.4% and 4.01% hydrogen alloys down to approximately 80 K. Evidence of hydride precipitation was found in the 2.4% and 4.01% alloys but not in the 0.94% alloy which confirms the internal friction results. This also indicates the phase boundary between hydrogen in solution and hydride occurs in the composition range 0.94% to 2.4% hydrogen for the 80V20Nb alloy.
Fig. 4.20. Internal friction results for the 90V10Nb alloy with various hydrogen concentrations.
Fig. 4.21. Internal friction results for the 80V20Nb alloy with various hydrogen concentrations. All results corrected to 270 Hz.
Because hydride precipitation was not found for hydrogen concentrations less than or equal to 0.94% hydrogen, the 0.6% hydrogen sample was examined at two frequencies to determine activation parameters for the hydrogen peak. The activation energy was found to be 0.193 eV with $\tau_0$ equal to $3.7 \times 10^{-14}$ sec. Note the $\tau_0$ agrees quite well with values found by Peterson et al. (48) as listed in Table V. The activation energy also follows the trends discussed in 4.3.1. and shown in Fig. 4.8.

DSA was also used to examine the activation energy change with various hydrogen concentrations. The results are listed in Table XIV and Fig. 4.22. Note that for the alloys containing up to 0.94% hydrogen, the activation energy decreases with increasing hydrogen and the activation energy distribution resembles that found in the 70V30Nb and 60V40Nb alloys. For the alloys containing 2.4% hydrogen or more the activation energy increase with increasing hydrogen due to the growth of the precipitate peak and the diminishing of the hydrogen Snoek peak. The activation energy distribution for the alloys with 2.4% hydrogen or more were found to be non-Gaussian as seen in Fig. 4.22.
Fig. 4.22. DSA results for the 80V20NB alloy. Envelopes are generated using Gaussian distribution function.
Table XIV. Activation energies as determined from DSA for the 80V20Nb alloy

<table>
<thead>
<tr>
<th>Hydrogen Concentration</th>
<th>H(eV)</th>
<th>T(K)</th>
<th>f(Hz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.08&lt;sup&gt;a&lt;/sup&gt;</td>
<td>0.209</td>
<td>106.03</td>
<td>252.94</td>
</tr>
<tr>
<td>0.23&lt;sup&gt;a&lt;/sup&gt;</td>
<td>0.200</td>
<td>105.42</td>
<td>260.52</td>
</tr>
<tr>
<td>0.60&lt;sup&gt;a&lt;/sup&gt;</td>
<td>0.183</td>
<td>97.38</td>
<td>243.80</td>
</tr>
<tr>
<td>0.94&lt;sup&gt;a&lt;/sup&gt;</td>
<td>0.178</td>
<td>91.74</td>
<td>273.13</td>
</tr>
<tr>
<td>2.4&lt;sup&gt;b&lt;/sup&gt;</td>
<td>0.187</td>
<td>93.06</td>
<td>273.13</td>
</tr>
<tr>
<td>4.01&lt;sup&gt;b&lt;/sup&gt;</td>
<td>0.211</td>
<td>95.92</td>
<td>241.64</td>
</tr>
</tbody>
</table>

<sup>a</sup>Hydrogen is in solid solution.

<sup>b</sup>Both hydrogen in solid solution and hydride precipitates are found.

From internal friction measurements performed on alloys where precipitation was observed, the following conclusions can be drawn:

1. Hydride precipitation was found for the 90V10Nb alloy using both internal friction and low temperature microscopy. No evidence of a Hydrogen Snoek peak was found for the compositions explored.

2. Evidence of both a hydride peak and hydrogen Snoek peak were found in the 80V20Nb alloy. Hydride precipitation occurs at hydrogen concentrations greater than 0.94% using both internal friction and low temperature microscopy. The
results indicate clearly the coexistence of hydrogen in solid solution and in the form of precipitates.

3. Analysis of the frequency shift of the hydrogen peak resulted in values of \( \Delta H \) and \( \tau_0 \) that agree with the trends found using diffusion measurements.

4. DSA of the hydrogen peak revealed Gaussian energy distributions that indicated the activation energy decreases with increasing hydrogen concentration as was found in the other alloys.

5. Occurrence of hydride precipitation caused the average activation energy to increase due to the higher activation energy of the precipitate peak. DSA analysis results in a non-Gaussian distribution.

6. The peak height increases linearly with hydrogen concentration until hydride precipitation is found. Even for the hydrogen concentrations were precipitates were found, the peak height may still be a valid measure of the amount of hydrogen left in solid solution.
5. CONCLUSIONS

1. Measurement of the entire internal friction spectrum of the V-Nb alloys required development of a computerized vibrating reed apparatus.

2. Analysis of the V-0.2% O + H, V-0.48% O + H and Nb-0.2% O + H alloys required development of a linear regression procedure which lead to the relaxation parameters listed in Tables I, II, III and IV. The oxygen Snoek peak in these alloys was found to be governed by a single relaxation process. Addition of hydrogen had no effect on the peak shape or peak position. Hydrogen also had no effect on the activation energy and \( \tau_0 \).

3. The hydrogen Snoek peak in V-Nb alloys was found to be broader than a single relaxation peak. To determine the distribution of the activation energies that govern the peak, Direct Spectrum Analysis (DSA) as developed by J.R. Cost (41-44) was used. From DSA, the activation energy was found to decrease with increasing hydrogen concentration. The hydrogen Snoek peak was also found to shift to lower temperature with increasing hydrogen concentration which also indicates a decreasing activation energy.

4. The peak height increases linearly with hydrogen concentration. V/Nb ratio was not found to affect the relaxation strength of the hydrogen Snoek peak.
5. Statistical analysis of the DSA results lead to determination of a, a measure of the width of the Gaussian distribution. a did not vary with hydrogen concentration or V/Nb ratio. It was found to be smaller than a obtained on hydrogenated amorphous metals measured by Kirchheim et al. (53). This indicates a broader hydrogen relaxation energy distribution in the amorphous metals than in the V-Nb alloys.

6. Analysis of the shift in temperature with frequency lead to activation parameters that followed the same trends Peterson et al. (48) found for hydrogen diffusion in the same set of base alloys. The values for activation energy found by internal friction were consistently higher than those found in diffusion. However, because of inaccuracies in determining the peak temperature, the possible error in the internal friction values is ±0.03 eV. Because the internal friction measurements were made at lower temperatures than the diffusion measurements, the higher activation energies may be the result of trapping of the hydrogen by the substitutional atoms. Verification of this is possible if Gorsky measurements are made.

7. The results for the V-Nb alloys show many similarities to those found in amorphous metals (53). It is believed that only hydrogen atoms at the Fermi energy of hydrogen contribute to the relaxation process in these alloys.
8. The deuterium internal friction peak was shifted to higher temperatures and was broader than the hydrogen Snoek peak which indicates a higher activation energy for deuterium than for hydrogen. This was confirmed by frequency shift results and DSA. This same trend was found in the diffusion measurements (48).

9. The deuterium Snoek peak was also broader than a single relaxation peak. DSA indicated a Gaussian distribution. Activation energy was also found to decrease with increasing deuterium concentration.

10. A linear relationship was found between the deuterium peak height and concentration. However, the deuterium relaxation strength was found to be higher than the hydrogen relaxation strength.

11. Addition of oxygen to 70V30Nb + hydrogen alloys had no effect on the hydrogen peak shape or the activation parameters. The relaxation strength was also unchanged by addition of oxygen. Therefore oxygen did not affect the relaxation due to hydrogen in the 70V30Nb alloy.

12. A hydride precipitation peak was found in the 90V10Nb alloy using internal friction. This was verified by low temperature microscopy.

13. Evidence of both hydride precipitation and hydrogen in solution was found in the 80V20Nb alloy. Analysis of the frequency shift and DSA of the hydrogen peak resulted in
values of $H$ and $\tau_0$ that agree with the trends found in diffusion measurements. Occurrence of hydride precipitation does affect the DSA results, resulting in a non-Gaussian distribution.
6. BIBLIOGRAPHY


7. ACKNOWLEDGMENTS

I would like to express my appreciation to Dr. Otto Buck for his continued support and guidance in preparation of this thesis. His encouragement and interest have made my research experience a very rewarding one.

The technical assistance and friendly encouragement of C.V. Owen and D.K. Rehbein are also greatly appreciated. In addition I would like to thank the other graduate students and group members who have made my work more enjoyable.

A special thanks goes to my parents who instilled in me the desire to learn and to my husband, Michael, for his support and understanding. During the past three years he has made the bad times bearable and the good times better. It is my hope that our child will also understand the value of an education and that he has found his experience with higher education an enjoyable one.