ENGINEERING AND INDUSTRIAL EXPERIMENT STATION

College of Engineering

University of Florida

Gainesville
DEFORMATION PROCESSES IN REFRACTORY METALS

Progress Report

R. W. Arey, F. Boratto,
D. E. Wise, P. G. Watson,
and R. E. Reed-Hill

University of Florida
Gainesville, Florida 32611

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ABSTRACT

In the period covered by this report, two papers were published. The abstracts of these papers are given in sections 1 and 2 below. Four others have been accepted for publication and are abstracted in sections 3 through 6. In addition to this, Mr. Juan Donoso has published his dissertation which is summarized in section 8. A paper has been prepared for presentation at the "Interstitial Effects in Refractory Metals" session of the Fall AIME meeting in Niagara Falls, New York. This is outlined in section 7.

Other work currently underway is discussed in sections 9 through 12. This includes (section 9) new internal friction determinations of the diffusion coefficients of O and N in niobium and a re-evaluation of the available relevant data in the literature. We believe that the results of this study make it possible to rationalize apparent inconsistencies in the literature.

Section 10 represents a paper that is in preparation for publication on the subject of static strain-aging in titanium. It is based on a portion of Dr. Donoso's dissertation.

Section 11 constitutes a review of our work on the effect of hydrogen on the yield point phenomena in niobium at the temperatures 273 K and 193 K. Finally, section 12 describes our transmission electron microscopy work on titanium, whose primary goal has been to obtain a better insight into the causes of anomalous work hardening associated with dynamic strain-aging in this metal.
A. PAPERS PUBLISHED OR ACCEPTED FOR PUBLICATION


The embrittlement of niobium has been studied over the temperature range from 77 to 1100 K using tensile specimens containing between 0.09 and 2.31 at. pct oxygen. A slow strain-rate embrittlement was observed in specimens containing more than 0.5 at. pct oxygen that occurred inside the approximate temperature range from 500 to 1000 K. In analogy with the slow strain-rate embrittlement due to hydrogen, a ductile-to-brittle-to-ductile fracture transition was observed; the ductility (reduction in area) decreased with decreasing strain-rate; the ductility decreased with increasing oxygen concentration; and a fracture morphology involving both intergranular and transgranular modes was observed. The transgranular mode, which was the predominant one, resembled cleavage.


The determination of the internal component of the flow stress in a material may be made by using several methods. Some of the most used, which involve stress relaxation, are the continuous relaxation analysis of Gupta and Li, and incremental unloading. As indicated by Guiu, the relaxation inherent in a tensile
The testing machine can seriously influence the determination of the internal stress by either of these two methods. In this study, the Instron relaxation was evaluated at room temperature, and the data obtained from tests on commercial purity titanium were corrected for this relaxation. It was proposed that the basic shape of an incremental unloading curve is strongly dependent on both the relative magnitude of the internal stress as well as on the value of $m^*$, the dislocation velocity exponent, and that it differs substantially from those reported in the literature. The situation becomes more complicated in a material like commercial purity titanium, where dynamic strain-aging effects due to hydrogen are possible at room temperature at strain-rates of the order of those normally associated with stress relaxation.


The basic principles involved in thermal activation analysis at low temperatures are reviewed. The definitions of the activation parameters in terms of quantities that can be determined from experiments are reviewed. Without referring to any specific mechanism, the causes for some of the shortcomings of activation analyses are sought in terms of the inherent limitations in accuracy of the measurements and of phenomena that complicate deformation. It appears that the latter, namely dynamic strain-aging and mechanical twinning, may account for many failures of thermal activation analyses.
Static strain-aging was investigated in Nickel 200 using tensile specimens aged between 373 and 473 K. The kinetics of the lower yield stress return may be described in terms of either a $t^{1/7}$ or a log $t$ relationship. The activation energy for the process was about 25,000 cal/mole. It is believed, as proposed by Rose and Glover and by Jenkins and Smith for austenitic stainless steels, that the aging phenomena are associated with carbon atom-vacancy pairs which undergo Sneed ordering in the stress fields of dislocations. Macroscopic hardening probably results from the growth of atmospheres of pairs around the dislocations as a result of the drift of vacancies toward the dislocations. However, the growth of these atmospheres should be a slow process because of the trapping of vacancies by the much less mobile vacancies. Finally, since the number of vacancies which were formed by the prestrain deformation greatly exceeds the thermal equilibrium concentration of vacancies, there should be a slow loss of vacancies to sinks. This can explain the fact that at long times pronounced overaging is exhibited.

Slow strain-rate embrittlement has long been associated with hydrogen in steels and, only more recently, with hydrogen in other metals. As predicted by Troiano, it has now been observed in transition metals due to an interstitial other than hydrogen. Some observations on the phenomenon as observed in the niobium-oxygen system are presented. Evidence for a slow strain-rate embrittlement of titanium due to oxygen is also presented. It is noted that the fracture mechanism in titanium is basically different from that observed in niobium due to either hydrogen or oxygen. In titanium, microvoid coalescence is observed under all conditions of testing, whereas in niobium, embrittlement involves cleavage and brittle intergranular fracture. Some predictions concerning the susceptibility of the group Va transition metals to slow strain-rate embrittlement due to oxygen, nitrogen and carbon are considered.

6. W. R. Cribb and R. E. Reed-Hill, "The Effect of Aging Under Stress on Strain-Aging in Nickel 200," short paper prepared for the Second International Conference on Mechanical Behavior of Metals. (In this work, Dr. Cribb's contribution was supported by the International Nickel Company, Dr. Reed-Hill's by ERDA.)

It has been well documented that aging under stress can enhance the yield
point return. This paper reports some new observations on the effect of aging under stress obtained with Nickel 200. Cylindrical tensile specimens were deformed at a crosshead speed of 5 mm/min at 273 K. This deformation rate and temperature permitted deformation to occur without complications due to serrations on the stress-strain curve. The magnitude of the yield stress increment was significantly larger in Nickel 200 than in higher purity Nickel 270. This indicates that the effect is due to carbon in solid solution. The rapidity of the aging suggests that it is associated with the Snoek ordering of carbon-vacancy pairs. It was also observed that unloading, after aging under stress, tended to erase the aging treatment. This fact supports evidence that dislocation rearrangements occur during unloading.

B. PAPER PREPARED FOR AIME MEETING


Interstitial solutes can produce both slow strain-rate embrittlement and dynamic strain-aging in refractory metals. Until recently, slow strain-rate embrittlement has been primarily associated with the presence of hydrogen. On the other hand, dynamic strain-aging studies have been more concerned with systems involving a refractory metal and either oxygen, nitrogen or carbon. Because
the activation energies for the diffusion of hydrogen in refractory metals are normally small, dynamic strain-aging phenomena due to hydrogen are expected to occur at very low subambient temperatures where the solubility of hydrogen is often very small. As a consequence, studies of dynamic strain-aging due to hydrogen have been limited. The recent observation of slow strain-rate embrittlement in niobium due to oxygen now allows a direct comparison between the two phenomena to be made on a single system. This is the primary goal of this paper.

C. DISSERTATION


Static strain-aging and slow strain-rate embrittlement were investigated in a commercial purity titanium, containing 0.4 at.% oxygen as the principle interstitial impurity. The experiments were conducted on 17 μM grain size specimens, prestrained 2% at a nominal 3.3 x 10^{-4} sec^{-1} strain-rate. Following prestraining, the specimens were immediately unloaded to about 10 MPa, and aged in situ between 555 and 630 K for various times. In this temperature interval,
deformation twinning and serrated flow were not observed. The return of both the upper and the lower yield stresses were observed as functions of time. Under the conditions employed, the strain-aging response of titanium appeared to consist of three stages: (1) an interval in which the yield point return was small and time-independent, probably associated with an unloading effect; (2) a region in which the yield point return parameters rose to a saturation plateau at intermediate aging times; and (3) a region where a further increase in the upper yield point occurred after the saturation plateau. The yield point return in stage (2) increased as \( t^{2/3} \), once correction for the unloading yield point effect was made. The activation energy for aging in stage (2) was 50,525 cal/mole, which is consistent with that for diffusion of oxygen.

The stress-strain behavior and the work hardening after aging were also analyzed, using empirical methods. The former was characterized in terms of the Swift equation, \( \varepsilon = \varepsilon_0 + cs^n \), parameters. The latter was normalized in terms of the ratios of the flow stresses of an aged and a control unaged specimen deformed at the same temperature. It was observed that significant changes in both the stress-strain behavior and the work hardening occurred in the third stage. It is speculated that aging in this stage is due to a second interstitial species (possibly nitrogen), and/or to dislocation rearrangements after aging.

Titanium is subject to a slow strain-rate embrittlement that depends on composition and strain-rate. However, dynamic recovery limits the embrittlement temperature range. Slow strain-rate embrittlement was not observed in a higher purity titanium (0.02 at.% oxygen).

The slow strain-rate embrittlement of commercial purity titanium was also
found to be dependent upon the grain size, the phenomenon being weaker the smaller the grain size. Decreasing the latter to a grain size of 6 μm eliminated the embrittlement. These observations can be rationalized in terms of enhanced dynamic recovery in the finer grain size commercial purity titanium. Dynamic recovery also has an effect on dynamic strain-aging in the fine grain size material.

D. REPORT OF WORK IN PROGRESS


INTRODUCTION:

In niobium the interstitial atoms which are primarily responsible for strain-aging are oxygen, nitrogen and carbon. Carbon, however, has a very low solubility in niobium and thus will not be considered here. A literature search on the subject of diffusion of oxygen and nitrogen in niobium has revealed several inconsistencies that can be summarized as follows:

1) Calculations of the entropy of activation for the diffusion of oxygen in niobium made by Beshers,¹ using the internal friction data of Powers and Doyle,² have indicated that the oxygen-niobium data are not in agreement with those of other systems. This could imply that the oxygen atoms are favoring occupancy of tetrahedral sites³ (in most b.c.c. metals it is believed that the
octahedral sites are preferred), or it could be possible that the Powers and Doyle data are not precise enough for this form of calculation.

2) Ogurtani and Uygur have made diffusion experiments on nitrogen in niobium and claimed that the activation energy for nitrogen diffusion in this metal decreases with temperature. This is in conflict with the usual concept of an Arrhenius behavior where the activation energy is assumed to be independent of the temperature.

In this work some new low temperature internal friction data are combined with high temperature diffusion measurements and with certain medium temperature high frequency internal friction data in order to obtain more information about the oxygen-niobium and nitrogen-niobium systems with the goal of shedding light on the two inconsistencies mentioned above.

INTERNAL FRICTION MEASUREMENTS:

The internal friction measurements were made on 80 mm long by 0.76 mm diameter niobium (MARZ grade) wires, surface cleaned and annealed in a dynamic vacuum better than 1.0E-3 Pa* at 1250 K for 90 minutes. The original nitrogen and oxygen concentrations were 0.003 at.% and 0.009 at.%, respectively, but the Snoek peak heights, \( d \) in Table 1, indicated higher values than these, probably because of contamination during the annealing treatment.

The torsion pendulum was a standard K\( \ddot{\text{e}} \) type with modifications for operation in vacuum and with a differential transformer pick-up connected to a Sanborn

*The notation 1.0E-X = 1.0 x 10^{-X} is used here.
Table 1: Oxygen and nitrogen Snoek peak parameters for diffusion constant calculations according to NOWICK and BERRY (1) technique.

**Oxygen**

<table>
<thead>
<tr>
<th>Freq. (Hz)</th>
<th>$Q_s$ (cal/mol)</th>
<th>$d_m$</th>
<th>$\tau$ (1/s)</th>
<th>$D_2$ (cm²/s)</th>
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<td>23480</td>
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<td>7.982E-17</td>
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<td>0.2712</td>
<td>1.116E-16</td>
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<td>0.927</td>
<td>23812</td>
<td>3.3E-3</td>
<td>0.1719</td>
<td>1.761E-16</td>
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</tbody>
</table>

**Nitrogen**

<table>
<thead>
<tr>
<th>Freq. (Hz)</th>
<th>$Q_s$ (cal/mol)</th>
<th>$d_m$</th>
<th>$\tau$ (1/s)</th>
<th>$D_2$ (cm²/s)</th>
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<td>30677</td>
<td>3.0E-3</td>
<td>0.1719</td>
<td>1.761E-16</td>
</tr>
</tbody>
</table>
recorder for automatic recording of data as in the model by Petarra. The specimens were heated by means of a three zone furnace with individual controls for each zone in order to obtain a zero gradient of temperature in the specimen. The temperature was measured by placing three thermocouples adjacent to the sample (one at each end and the third at the center). A first run, with the center thermocouple attached to the specimen, indicated that the temperature in the sample was about 7 K lower than the temperature indicated by the other two thermocouples, probably because of heat loss through the rods and inertia bar that were attached to the specimen. After the determination of a temperature calibration curve, the center thermocouple was separated from the sample and internal friction measurements were made only after an interval of at least 30 minutes in order to allow the temperature to stabilize.

SNOEK PEAK SHAPE ANALYSIS:

The Snoek peak can be described by the Debye Equation,

\[ d = d_m \cdot \exp \left( \frac{Q_s}{RT} - \frac{Q_s}{RT_p} \right) \]  

where \( d \) is the logarithmic decrement, \( Q_s \) the activation energy obtained by shape analysis as described below, \( T_p \) the temperature of the peak and \( d_m \) the logarithmic decrement at \( T_p \). As indicated by Nowick and Berry, the \( Q_s \) value is usually smaller than the real \( Q_r \) value obtained by frequency shift measurements. This has been rationalized as due to the existence of a distribution of relaxation times rather than a simple relaxation time. Nevertheless, Nowick indicated that the Snoek peak can be well described empirically by Eq. (1) in terms of
this "false" activation energy $Q_s$. Note that Eq. (1) can be written in the form

$$\text{arc cosh}(d_m/d) = \frac{Q_s}{RT} - \frac{Q_s}{RT_p}$$

therefore, a plot of arc cosh($d_m/d$) versus $1/T$ will yield a straight line whose slope is $Q_s/R$ and whose intercept is $Q_s/RT_p$. The oxygen and nitrogen internal friction data were presented in this form in Figs. 1 and 2, since the concentration of interstitials were low and the oxygen peak well separated from the nitrogen peak. The main advantage of using this type of plot is the ease with which one can read $T_p$.

Assuming that the interstitials occupy octahedral positions in the b.c.c. lattice and that diffusion occurs by jumps from one octahedral position to another adjacent octahedral position, it is possible to connect the diffusion constant $D$ with the relaxation time $\tau$ obtained at the Snoek peak in an internal friction experiment by the equation

$$D = \frac{a_o^2}{36\tau}$$

where $a_o$ is the lattice parameter. The necessary parameters for measuring $\tau$, as described in Ref. 7, are shown in Table 1. The resonance condition $\ln\omega\tau = 0$, where $\omega$ is the torsion pendulum frequency in rad/s, is modified to $\ln\omega\tau = \delta x$, where $\delta x$ is a correction for the peak location that depends upon the $Q_s/Q_\tau$ ratio and upon $d_m$. In the last column in Table 1 are shown $D$ values for oxygen and nitrogen diffusion calculated after Eq. (3) and with $\tau$ values from the modified condition $\ln\omega\tau = \delta x$. In Tables 2A and 3A, these $D$ constants are shown again.
Fig. 1. Shape analysis of the oxygen Snoek peak in niobium at three different frequencies.
Fig. 2. Shape analysis of the nitrogen Snoek peak in niobium at three different frequencies.
Table 2A: Low temperature oxygen diffusion data. Calculated from internal friction experiments.

<table>
<thead>
<tr>
<th>Point #</th>
<th>Freq. (Hz)</th>
<th>D (cm²/s)</th>
<th>Tp (°C)</th>
<th>ln D</th>
<th>1000/T (1/°K)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
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<td>1</td>
<td>.40</td>
<td>7.609E-17</td>
<td>140.0</td>
<td>-37.114</td>
<td>2.420</td>
<td>17</td>
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<tr>
<td>2</td>
<td>.483</td>
<td>9.191E-17</td>
<td>148.0</td>
<td>-36.926</td>
<td>2.374</td>
<td>19</td>
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<tr>
<td>3</td>
<td>.55</td>
<td>1.046E-16</td>
<td>140.0</td>
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<td>2</td>
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<td>1.0</td>
<td>1.902E-16</td>
<td>157.0</td>
<td>-36.198</td>
<td>2.325</td>
<td>8</td>
</tr>
<tr>
<td>6</td>
<td>1.433</td>
<td>2.727E-16</td>
<td>155.0</td>
<td>-35.838</td>
<td>2.335</td>
<td>19</td>
</tr>
<tr>
<td>7</td>
<td>2.133</td>
<td>4.059E-16</td>
<td>168.0</td>
<td>-35.440</td>
<td>2.267</td>
<td>19</td>
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<tr>
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<tr>
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<tr>
<td>14</td>
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<td>9.503E-12</td>
<td>370.0</td>
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Table 2B: High temperature oxygen diffusion data. Calculated from hardness profiles from indicated references using non-linear least square fitting program.

<table>
<thead>
<tr>
<th>Point #</th>
<th>$D$ (cm$^2$/s)</th>
<th>$T_p$ (°C)</th>
<th>$\ln D$</th>
<th>$1000/T$ (1/°K)</th>
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Table 3A: Low temperature nitrogen diffusion data. Calculated from internal friction experiments.

<table>
<thead>
<tr>
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<th>Freq. (Hz)</th>
<th>D (cm²/s)</th>
<th>Tp (°C)</th>
<th>ln D</th>
<th>1000/T (1/°K)</th>
<th>Ref.</th>
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Table 3B: High temperature nitrogen diffusion data. Transcribed from indicated references without modifications.

<table>
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<tr>
<th>Point #</th>
<th>D (cm²/s)</th>
<th>Tp (°C)</th>
<th>ln D</th>
<th>1000/T (1/°K)</th>
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<td>-15.307</td>
<td>.785</td>
<td>4</td>
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<tr>
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<td>.728</td>
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<tr>
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<td>1200.</td>
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</tr>
<tr>
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<td>1300.</td>
<td>-13.663</td>
<td>.636</td>
<td>4</td>
</tr>
</tbody>
</table>
as well as certain reported values of other authors. Items 1 to 7, in both tables, are low frequency data from five different authors. While the frequencies are arranged in increasing order, the same trend is not observed in $T_p$, as should occur. Several reasons could be advanced to explain this, such as a high interstitial concentration, a gradient of temperature in the specimen or a temperature dependent background. The points 1 to 7, therefore, were not used in the minimum least square fit in the Arrhenius plots of Figs. 3 and 4, although they are shown in the figures as "other" points. The points 11 to 14 in Table 2A and points 11 to 13 in Table 3A are high frequency internal friction data from three different authors. Again, only the more recent, Ref. 12 and 13, were used in the straight line calculations, but data points from Ref. 14 are shown in the figures as a matter of comparison.

HIGH TEMPERATURE DIFFUSION MEASUREMENTS:

The high temperature data on nitrogen diffusion in niobium is shown in Table 2B and Fig. 4, as it is reported in the references. However, the oxidation data were reanalyzed and only the corrected data is shown. The new analysis is as follows:

The Fick's second law for an oxidation process at constant temperature, assuming a diffusivity that is independent of concentration and a fixed oxide-metal interface, is

$$\frac{C_x - C_b}{C_s - C_b} = \text{erfc} \left( \frac{x}{2\sqrt{Dt}} \right)$$

where $C_b$ is the concentration in the bulk (original concentration), $C_s$ the con-
Fig. 3. Arrhenius plot of oxygen diffusion data in niobium.
Fig. 4. Arrhenius plot of nitrogen diffusion data in niobium.
centration at the surface and $C_x$ the concentration at the point $x$.

The hardness of niobium is an almost linear function of the oxygen concentration; thus, one can substitute the hardness for the concentration in Eq. (4) and write

$$
\frac{H_x - H_s}{H_s - H_b} = \text{erfc}\left(\frac{x}{2\sqrt{Dt}}\right)
$$

(5)

Therefore, a hardness profile ($H_x$ versus $x$) can be used to calculate $D$, provided that $H_s$ is known. Values of $H_s$ are experimentally difficult to obtain and usually they are estimated by graphical extrapolation methods. To avoid these extrapolation methods and to get better accuracy in the $D$ calculations, a non-linear least square fitting program, written by Professor C. D. Kylstra, Department of Nuclear Engineering Sciences, University of Florida, was used. The program was modified to use Eq. (5) as the equation to be optimized, with the parameters $D$ and $H_s$ left as adjustable parameters. A typical result is shown in Fig. 5 where the curve is drawn according to Eq. (5) using the indicated parameters. All three high temperature points in Table 2B were calculated this way.

A linear least square fit on the "best" values in Figs. 3 and 4 yields

$$
D = 0.01\exp(-26580/RT)
$$

(6)

$$
D = 0.03\exp(-36660/RT)
$$

(7)

for the oxygen and nitrogen diffusion in niobium, respectively. Although the resulting activation energies do not differ appreciably from previous published results, the $D_0$ values are very different. Accurate values of $D_0$ are of importance for entropy of activation calculations and for a test of Wert and Zener's theory.
Fig. 5. Vickers hardness number VHN (kg/mm²) as a function of distance from the surface X in an oxidized niobium sample. Data points from Ref. 22 and theoretical curve according to Eq. (5) after non-linear least square optimization.
ENTROPY OF ACTIVATION CALCULATIONS:

In the latest check of Wert and Zener's theory in a paper by Beshers, the niobium systems showed some discrepancies. The following is a recalculation of entropy of activation $\Delta S^*$ using the just-calculated $D_o$ and $Q_r$ values, following closely the Beshers paper.

The entropy of activation is given by

$$\frac{\Delta S^*}{k} = \ln\left[\frac{3 \frac{D_o}{2}}{2v(a_o/2)^2}\right]$$

where $v$ is the vibrational frequency given by

$$v = \left[\frac{E}{2m(a_o/2)^2}\right]^{1/2}$$

and where $m$ is the mass of the interstitial atom and $E$ the activation energy in ergs.

Using values of $a_o$ recently calculated, the $v$ and $\Delta S^*/k$ values are

$v = 1.116 \times 10^{13}\ \text{1/s};\ \Delta S^*/k = 1.596\ \text{ (oxygen)}$

$v = 1.402 \times 10^{13}\ \text{1/s};\ \Delta S^*/k = 2.467\ \text{ (nitrogen)}$

In Wert and Zener's theory, $\Delta S^*$ can be calculated, with the assumption that the energy of activation goes into straining the lattice, through the following expression:

$$\Delta S^* = \frac{\beta E}{T_m}$$

where $T_m$ is the melting temperature of the metal and $\beta$ a constant whose value is 0.51 for the niobium lattice.

Defining a parameter $\lambda = (\Delta S^*/k)(kT_m/\beta E)$ it is possible to compare the
values obtained in this study with those obtained by Beshers. The $\lambda$ values are 0.64 and 0.72 for the oxygen and nitrogen, respectively. These values are quite different from the 0.97 and 0.37 obtained by Beshers where the activation energies and frequency factors from Ref. 2 were used. As indicated previously, the $D_0$ values in Ref. 2 are not in agreement with those presently obtained. The present values of $\lambda$ are also in agreement with the average value of 0.55±0.20 obtained by Beshers for eleven different systems as well as with the more refined theory of Keyes$^{25}$ as was pointed out in Ref. 1.

CONCLUSIONS:

Diffusion coefficients of nitrogen and oxygen in niobium, calculated using internal friction technique assuming octahedral occupancy, are in good agreement with coefficients of diffusion calculated by high temperature direct measurements. Both oxygen and nitrogen diffusion coefficients follow an Arrhenius type of behavior and the energies of activation were not found to vary with temperature in opposition to the claims of Ogurtani and Uygur$^4$ for the nitrogen-niobium system.

Discrepancies found in the oxygen-niobium system, when only the internal friction data of Powers and Doyle$^2$ were used, were eliminated when the combined high temperature diffusion and internal friction data were used. The calculated entropy of activation values are in agreement with those of eleven other systems measured by Beshers$^1$ and with the model of Keyes.$^{25}$
Abstract

Static strain-aging was investigated in commercial purity α-Ti, containing 1360 ppm by weight of oxygen as the principal interstitial impurity. Aging was conducted in situ on 17 μM grain size specimens, prestrained to 0.02 strain at a nominal strain-rate of $3.3 \times 10^{-4}$ s$^{-1}$, between 555 and 630 K for various lengths of time. The increase of both the upper and the lower yield stresses were employed as measures of the aging progress, and used in the evaluation of the aging kinetics. Under the conditions employed, the static strain-aging response of titanium appeared to consist of four stages, of which only stages 1 and 2 were considered in this work. Stage 1 corresponded to an "unloading" type of yield point, while stage 2, after correcting for the time-independent increase in the yield point of stage 1, conformed closely to Cottrell aging, i.e., the increase in flow stress after aging followed a $t^{2/3}$ behavior. The activation energy deduced for the process, following a method developed by Hartley, is in good agreement with that reported for the diffusion of oxygen in titanium.

Introduction

Titanium is a metal whose mechanical properties are strongly influenced by the presence of interstitials in solid solution. Although several investigators have demonstrated that interstitials produce strain-aging effects in
this metal, an investigation of the kinetics and energetics of static strain-aging in titanium has been lacking. This paper reports on such a study undertaken using a commercial purity titanium.

Experimental Procedures

The titanium used in this investigation was purchased from Reactive Metals, Inc., as rolled plate. Its principal impurities in ppm by weight were Fe-1600, O-1360, C-200, N-100 and H 54/92. Square bars of approximately 1.0 by 1.0 cm in cross-section were cut from the plate parallel to its rolling direction and were swaged directly to 0.55 cm diameter cylindrical rods. Threaded-end tensile specimens were machined from the rods. These were annealed under a dynamic vacuum of about $10^{-5}$ Torr at 1073 K for 30 minutes to produce an equiaxed grain structure with a mean linear intercept of 17 μm. The gage sections of the tensile specimens had a nominal diameter of 0.36 cm and a length of 2.54 cm.

Static strain-aging experiments were conducted in situ at four temperatures, 555, 575, 600 and 630 K. All tests were made under a high purity, oxygen-gettered argon atmosphere in order to minimize specimen contamination. A standard cross-head speed of 0.051 cm/min was used, which corresponded to a nominal strain-rate of $3.3 \times 10^{-4}$ s$^{-1}$. The tensile specimens were prestrained before aging to 0.02 strain. When this prestrain was reached, the specimens were unloaded to a stress of about 10 MPa in order to maintain alignment in the tensile jig. They were then aged in situ for various lengths of time ranging from 150 seconds to about $2.55 \times 10^5$ seconds (68 hours). The recorded aging time was measured from the instant that the unloading of the specimen was started to that time.
at which the load of the reloading curve reattained the value of the preload.

In the reloading part of the experiment, the majority of the specimens were deformed to fracture. The aging temperature, measured by means of a thermocouple inserted in the testing capsule, could be maintained to within ±1 K for periods of less than 5000 seconds, and to within ±2 K for longer times.

The principal parameters employed in the evaluation of the kinetics of the yield point return were $\Delta \sigma_u$ and $\Delta \sigma_l$, the upper and lower yield point increments, respectively. These are defined in Fig. 6. The hardening component $\Delta \sigma_f$ or the indicated increase in the level of the flow stress after aging, which is also defined in Fig. 6, was not evaluated. This was due to the fact that at the start of the reloading curve, a transient stage with a very high work hardening rate was observed in many cases. Extrapolation of the slope of this initial part of the reloading curve normally resulted in a stress smaller than the pre-stress. Under these circumstances, it was felt that $\Delta \sigma_f$ was not meaningful.

Experimental Results

The parameters $\Delta \sigma_u$ and $\Delta \sigma_l$ that were employed as measures of the progress of aging are plotted as functions of the time for several temperatures in Figs. 7 and 8, respectively. In general, the aging curves in Fig. 7, which show the magnitude of the upper yield point return as a function of temperature, are consistent with a curve like that shown schematically in Fig. 9. Practical considerations did not permit a complete curve of this shape to be obtained at any of the four temperatures that were investigated. At the higher temperatures, the time required to unload and then reload the specimen set a
Fig. 6. Schematic showing the yield point increments employed in the evaluation of the aging kinetics in titanium.
Fig. 7. The time-temperature dependence of the return of the upper yield stress in commercial purity titanium. Specimens prestrained 2%.
Fig. 8. The time-temperature dependence of the return of the lower yield stress in commercial purity titanium. Specimens prestrained 2%.
Fig. 9. Hypothetical aging behavior in titanium in the light of the results shown in Fig. 7.
minimum aging time that was longer than that required to reach the second stage so that the initial stage of the curve was effectively eliminated. At the lower temperatures, the maximum aging time, 250,000 s, that it was feasible to use for aging on the Instron, was not long enough to reveal all of the later stages of the aging curve. Note that Fig. 7 shows an initial stage in the $\Delta\sigma_u$ versus log t curve that is apparently time independent in which $\Delta\sigma_u = 4.0 \pm 0.2$ MPa. The existence of this stage is evident in both the 555 and 575 K curves of Fig. 7. This stage is also apparent in the 555 and 575 K curves of Fig. 8, which show the lower yield stress increment, $\Delta\sigma_1$, as a function of the aging time. Such a stage implies an "unloading" type of yield point similar to that observed by Haasen and Kelly in fcc metals. As a test of this hypothesis, an aging experiment was conducted at 600 K, in which the specimen was unloaded and immediately reloaded. This also resulted in the same yield point increment of about 4.0 MPa. It is also important to note that Malik and Dickson have previously identified a Haasen and Kelly unloading yield point in titanium between 300 and 423 K. The present observation extends the ranges of temperatures where this type of phenomenon has been observed into the 550 and 630 K interval.

In order to determine the time dependence of the dynamic component of the aging process that appears at the end of the first plateau or in Stage 2, observed values of $\Delta\sigma_u$ and $\Delta\sigma_1$ were corrected for the initial time independent stress. To do this, the differences $\Delta\sigma_u - \sigma_o$ and $\Delta\sigma_1 - \sigma_o$ were plotted against time on double logarithmic coordinates as shown in Figs. 10 and 11, where $\sigma_o$ represents the value of the initial, time independent yield point return. The slopes of these curves as obtained using a least squares analysis are indicated on
Fig. 10. The time-temperature dependence of the return of the upper yield stress of Fig. 7, corrected for the initial, time independent stress. The slopes of the lines in double log coordinates are indicated in the figure.
Fig. 11. The time-temperature dependence of the return of the lower yield stress in Fig. 8, corrected for the initial-time independent stress. The slopes of the lines in double log coordinates are indicated in the figure.
the figures. The slopes range between 0.60 and 0.72 at the three lower temperatures, while at 630 K, the highest temperature, the slope was about 0.40. These results were essentially independent of whether one considers the upper field point increment, $\Delta \sigma_u$, in Fig. 10, or the lower yield point increment in Fig. 11.

From the above, it would appear that over the temperature range from 555 to 600 K, the return of the yield point immediately following the initial time independent plateau can be described by the relation

$$\Delta \sigma = \Delta \sigma_0 + \gamma t^{2/3}$$  \hspace{1cm} (11)

where $\Delta \sigma$ represents the increase in either the upper or lower yield points, and $\gamma$ is a constant. In confirmation of this conclusion, Fig. 12 shows that plots of $\Delta \sigma_u - \Delta \sigma_d$ as a function of $t^{2/3}$ give reasonably straight lines at 600, 575 and 555 K, respectively.

Fig. 9 also indicates that there is a second plateau followed by a second rise in the $\Delta \sigma_u$ parameter at long times. These features are designated as Stages 3 and 4 in Fig. 9. These stages are observed in the curves obtained at the two higher temperatures, 630 and 600 K. Due to the lack of sufficient data points in this region, no attempt was made to analyze this region. Thus, strain-aging refers here to the initial rising part, in Stage 2, of either the $\Delta \sigma_u$ or the $\Delta \sigma_d$ against time curves.

It should be noted that the lower yield stress increment does not apparently undergo a second rise (Stage 4). On the other hand, $\Delta \sigma_1$ does pass through a second plateau (Stage 3).
Fig. 12. The corrected upper yield stress return vs. $t^{2/3}$ at the three lower temperatures. Data for the 630 K case (not shown) do not fit the $t^{2/3}$ relation.
In order to establish a mechanism for the strain-aging process in Stage 2, an empirical activation energy was deduced as follows. Arrhenius plots of the time needed to reach a given stress versus the reciprocal of the aging temperatures were determined at values of $\Delta \sigma_u - \Delta \sigma_o$ equal to 3, 5 and 10 MPa and of $\Delta \sigma_1 - \Delta \sigma_o$ of 3 and 5 MPa, respectively. Fig. 13 shows these Arrhenius plots. As can be observed, the 630 K data points do not fit the behavior followed by the data obtained at the three lower temperatures. This could be due to the fact that the aging times were short at the highest temperature and that accelerated aging during the unloading and reloading of the specimen biased the data. During each unloading and reloading cycle, the specimen was subjected to aging under a stress of varying magnitude. A time interval of about 25 secs was required to either unload or reload the specimen. During these time increments, the specimen was aging under a variable load. It has been demonstrated by a number of authors that aging under stress, particularly a stress close to the flow stress, can accelerate the aging process. The aging effects developed during these time intervals are probably insignificant if the total aging time is large, and if the temperature is low enough so that only a Haasen and Kelly unloading yield point effect was observed. However, for short aging times, they may be significant. Errors arising from this source may be largely responsible for the fact that the 630 K (highest aging temperature) data were inconsistent with those obtained at the three lower temperatures.

Thus, the 630 K data were ignored and the activation energy in each case was computed using only the data for the three lowest temperatures. The calculated average was 50,500 cal/mole, with a standard deviation of ±1,100 cal/mole.
Fig. 13. Arrhenius plots of the times to achieve a given value of the parameters $\Delta \sigma_u - \Delta \sigma_o$ and $\Delta \sigma_1 - \Delta \sigma_o$. 

- ▲ $\Delta \sigma_u - \Delta \sigma_o = 3$ MPa
- ○ $\Delta \sigma_u - \Delta \sigma_o = 5$ MPa
- ▼ $\Delta \sigma_u - \Delta \sigma_o = 10$ MPa
- ● $\Delta \sigma_1 - \Delta \sigma_o = 3$ MPa
- △ $\Delta \sigma_1 - \Delta \sigma_o = 5$ MPa
The activation energy was also computed in terms of the temperature dependence of the coefficient $\gamma$ of Eq. (11) which equals the slope of the lines in Fig. 12. By an analysis due to Hartley, $^{35,36}$ $\gamma$ should be proportional to $(D/T)^{2/3}$, or

$$\gamma T_a^{2/3} \propto [D_o \exp (-Q/RT_a)]^{2/3}$$  \hspace{1cm} (12)

In this relation, $T_a$ is the aging temperature, $R$ the gas constant, and $D_o$ and $Q$ the frequency term and activation energy for diffusion of the interstitial responsible for the aging, respectively. Thus, a plot of $\ln(\gamma T^{2/3})$ vs. $1/T$ should yield a slope equal to $-2Q/3R$. The corresponding plot is shown in Fig. 14, where the slope is $-17,250$ cal/mole. Since the activation energy equals approximately three times the slope, the activation energy by this method is $51,750$ cal/mole.

Discussion and Conclusions

At least four different mechanisms have been postulated to explain strain-ageing in metals and alloys. These include the formation of Cottrell atmospheres, $^{37,39}$ Snoek ordering, $^{40,41}$ Suzuki locking, $^{42}$ and the precipitation of solute on dislocations. The latter two mechanisms are considered to be inapplicable in the present investigation. First, Suzuki locking has its origin in a chemical interaction between solute atoms and a stacking fault, and is only expected to be significant in metals of low stacking fault energy in which the stacking fault widths are large, as in Ag-6 wt.% Al. $^{43}$ In titanium, there are no experimentally determined figures available for the stacking fault energy;
Fig. 16. The quantity $y T^{2/3}$ as a function of the inverse of the aging temperature.
it is, however, expected to be high. Also, the yield stress should not be affected by thermal activation in Suzuki's mechanism. This is not the case of titanium, in which interstitials increase the thermally activated component of the flow stress, and the rate controlling thermally activated process in deformation below about 600 K, has been suggested to be the overcoming of interstitial barriers. Precipitation at dislocations, as a result of the segregation of solute, would also appear to be inappropriate due to the high solubility of oxygen in titanium (i.e., about 32 at.% in the temperature range in question). Precipitates were not observed in thin foil electron microscopy photographs made from specimens aged 4000 and 55,000 s at 630 K, respectively.

Of the remaining two mechanisms, Snoek pinning of dislocations by paired defects has been invoked as an applicable mechanism in hcp metals. In α-Zr, de Paula e Silva et al. experimentally determined the time for the $\Delta\sigma_f$ component in Fig. 6 to reach saturation. From diffusivity data, they estimated the average distances travelled by a diffusing oxygen atom in zirconium at the various aging temperatures. Since the calculated distances were between 2 and 3 Å, they concluded that Snoek pinning by pairs (oxygen-oxygen atom or oxygen-substitutional atom pairs) could explain their results. However, they did not undertake a kinetic study. Kelly and Smith have also investigated strain-aging in Zr-O alloys. Although they did not evaluate the activation energy associated with aging, they proposed that oxygen-oxygen pairs were responsible for the aging.

In Zircalloy-2, Veevers and co-workers have postulated that oxygen is the element responsible for strain-aging. In one case, they observed that
the increase in magnitude of the relative yield point did not follow a $t^{2/3}$ relation. In another paper, Veevers and Snowden concluded that strain-aging in Zircalloy-2 was due to oxygen-oxygen pairs.\(^{52}\)

Apparently, the basis to deduce that pinning in hcp metals and alloys is due to pairs lies in the fact that measurable anelastic phenomena in these materials is believed to arise when the interstitial is paired to another interstitial, or to a substitutional element.\(^{53-57}\) This is based on the assumption that a single interstitial causes a nearly isotropic distortion in the lattice, and that to produce a defect with a tetragonal strain field it is necessary to have a pair. However, anelastic effects and dislocation pinning are not necessarily related.\(^{58}\) The drift of impurities in the stress field of a dislocation is related to the hydrostatic pressure gradient and does not require that a defect be tetragonal. Thus, though one should not rule out completely the possibility of a small contribution to the observed yield point return due to Snoek pinning by pairs in titanium, this mechanism cannot account entirely for the observed locking as has been suggested in previous investigations.\(^{48-49,52}\)

The kinetics observed in the present investigation are in good agreement with Cottrell aging,\(^{37,38}\) and with Hartley's model.\(^{35,36}\) In the latter, it is shown that the increase in flow stress after aging, measured by $\Delta \sigma_u$ or $\Delta \sigma_1$ of Fig. 6, follows a $t^{2/3}$ behavior. It should be noted that in the present case, the $t^{2/3}$ behavior is only observed after correcting for the time-independent yield point return. The latter, which has the characteristics of an unloading yield point,\(^{27}\) has been previously observed in titanium at temperatures below 423 K.\(^{28}\) Also, the temperature dependence of the coefficient of the $t^{2/3}$ term
of Eq. (11) should yield the activation energy for the aging process. The value obtained for $Q$, 51,750 cal/mole, is in good agreement with that reported for the diffusion of oxygen in titanium.\(^{59-62}\) It would thus appear that the initial rise in flow stress in titanium is controlled primarily by the drift of oxygen atoms to dislocations, conforming closely to Cottrell aging, as deduced from an analysis of the data in a manner similar to that suggested by Hartley.\(^{35,36}\)
In 1960, Wilcox and Huggins\textsuperscript{63} reported yield point return data that they associated with the presence of hydrogen in niobium. The activation energy which resulted from an analysis of their yield point return data was 10,500 cal/mole. At that time this value was in good agreement with Albrecht, Goode and Mallett's\textsuperscript{64} activation energy for the diffusion of hydrogen in niobium. This value was obtained from data in the temperature range from 873 to 973 K using an adsorption method. In recent years it has been observed that there is a great deal of scatter in the measurement of the diffusivity of hydrogen in BCC refractory metals. This has been discussed by Birnbaum and Wert.\textsuperscript{65} They attribute this largely to surface effects in methods such as the adsorption technique and to trapping of hydrogen atoms by other interstitials present in the materials that were available for use in the early diffusion determinations.

More recent, improved techniques have indicated that the activation energy for the diffusion of hydrogen in niobium is much smaller than 10,500 cal/mole. A more reasonable value would appear to be of the order of 2250 cal/mole.\textsuperscript{66}

This large difference between the activation energy for the return of the yield point in hydrogenated niobium and that for the diffusion of hydrogen in niobium suggests that the Wilcox and Huggins\textsuperscript{63} yield point return phenomena merit further study. This section is primarily concerned with the preliminary results of such an investigation. Specifically, these include an energetics
study of the return of the yield point using hydrogenated niobium specimens
and an investigation of the effects of hydrogen on the deformation behavior
of niobium.

The material used in this work was MARZ grade niobium supplied by the
Materials Research Corporation. An analysis of this material is shown in
Table 4. The material was supplied in the form of 0.635 cm diameter rods, which
were swaged to a diameter of 0.475 cm and machined into cylindrical tensile
specimens with a gage length of 1.27 cm and a gage section diameter of 0.318
cm. The specimens were then annealed in a dynamic vacuum of $<10^{-5}$ Torr for
30 minutes at 1393 K to produce an equiaxed grain size of 100 $\mu$m.

The hydrogen charging technique employed in this study was based on a
method used by Ravi and Gibala, and involves cathodic charging of tensile
specimens in an electrolytic cell containing a 10% $\text{H}_2\text{SO}_4$ electrolyte. The speci-
mens were masked using a non-conductive coating, except for the gage length
surface area, and inserted in the cell with a platinum anode. Charging was
performed at a constant, monitored current density with the amount of hydrogen

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<td>-</td>
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</table>

Analysis 1 performed by the Materials Research Corporation.
Analysis 2 performed on an in-house Leco Hydrogen analyzer.
Analysis 3 performed by National Spectrographic Laboratories.
adsorbed by the specimen controlled by varying the charging time. Using a current density of 0.5 Amps/cm², it has been possible to introduce up to 14 wt ppm hydrogen in a four minute charging period, and to obtain a nearly linear correlation between the time of charging and the amount of hydrogen introduced into the specimen.

THE EFFECT OF OXYGEN ON THE YIELD POINT

An initial yield point was observed in the MARZ grade niobium in the as-received condition at about 380 K that increased in size as the testing temperature was decreased to 193 K, the lowest test temperature used in this study. The general form of this yield point (A) is shown in Fig. 15, where it is compared with the yield points from (B) the hydrogen charged niobium specimens of Wilcox and Huggins, and (C) VP niobium specimens also obtained from Materials Research Corporation. In all three of the materials sketched in this figure, oxygen is the main interstitial impurity. The oxygen contents are 60, 117, and 180 wt ppm for the MARZ niobium, Wilcox and Huggins' niobium specimens, and the VP niobium, respectively. It can be seen from Fig. 15 and the oxygen content data that the slope of the yield drop becomes steeper as the oxygen impurity content increases. In other words, the stress drops more precipitously the higher the oxygen concentration. This is to be expected if the yield point is due to pinning by residual oxygen in the niobium.
Fig. 15. This diagram shows the effect of oxygen on the initial yield point of niobium. The three curves correspond to (A) MARZ grade niobium, 60 ppm oxygen; (B) niobium used by Wilcox and Huggins, 117 ppm oxygen; and (C) VP grade niobium, 180 ppm oxygen.
THE EFFECT OF HYDROGEN ON THE INITIAL YIELD POINT

During the course of the yield point return experiments, it was observed that charging up to 17 wt ppm of hydrogen into the specimen has no perceptible effect on the initial yield point. This observation includes tests where, after charging with >8 wt ppm of hydrogen, the specimens were aged at temperatures in the range from 433 to 453 K with no discernible change in the initial yield point behavior.

THE RETURN OF THE YIELD POINT IN HYDROGEN CHARGED SPECIMENS

After charging, the specimens were prestrained 4% at 277 K. They were then removed from the testing jig and aged in a constant temperature silicone oil bath for predetermined periods of time. After aging, the specimens were then returned to the testing jig and restrained 1% at 277 K. Following this, the specimens were aged and restrained through several more cycles up to a total strain of 10%. At least 24 hours were allowed after charging and prior to any mechanical testing to allow sufficient time for internal hydrogen equilibration to occur. Analyses for hydrogen also indicated that no significant hydrogen loss occurred during high temperature aging at temperatures less than 480 K for the aging times employed. Due to the lack of reproducibility of the stress level at the upper yield point, particularly when the specimens are not aged in the testing jig under load, the event chosen to represent the yield point return was the smallest time at which a yield drop was discernible. This yield point event is shown in relation to the development of the yield point in Fig. 16.
Fig. 16. The effect of aging time on the shape of the yield point in MARZ niobium. Specimens strained at 277 K and aged at 433 K. The yield event used in the determination of an activation for yield is indicated on the diagram.
The first several specimens used in the yield point return procedure were not charged with hydrogen. This was done in order to characterize the yield point in the base material. The aging periods were carried out at temperatures between 403 and 435 K. The logarithm of the aging times to produce the yield event indicated in Fig. 16, and the corresponding reciprocal of the temperatures are plotted in Fig. 17. This figure shows that an Arrhenius relationship exists. For the equation of the form

\[ \frac{1}{t} = \alpha \exp(-Q/RT) \]  

(13)

where \( t \) is the aging time, \( T \) the aging temperature, \( Q \) the activation energy and \( R \) the gas constant, the data in Fig. 17 give a least mean squares fit activation energy of 26,300 cal/mole. This value is in very good agreement with the activation energy for the diffusion of oxygen in niobium as obtained by internal friction techniques.\(^2\,^{20}\) Thus, it would seem that residual oxygen is the primary pinning agent in this high purity material. A series of yield point return experiments were next carried out on three groups of specimens charged with hydrogen for 1.0, 1.5, and 2.0 minute periods, corresponding to hydrogen concentrations of approximately 4, 6 and 8 wt ppm, respectively. The data for these experimental runs were also plotted in Fig. 17. Two trends appear in this data which will be discussed. The activation energy is seen to remain constant for hydrogen concentrations up to 4 or 5 wt ppm, and then decrease from about 25,000 cal/mole to 13,000 cal/mole at 8 ppm of hydrogen. This indicates that an interaction between oxygen and hydrogen may be altering the energetics of the pinning process. Wilcox and Huggins,\(^6\) in their yield point
Fig. 17. Plots of the logarithm of the aging time needed for the appearance of the yield event against the reciprocal of the absolute temperature for MARZ grade specimens containing four levels of hydrogen.
return experiment, used niobium specimens containing 8 wt ppm hydrogen and 117 wt ppm oxygen, and obtained an activation energy of 10,500 cal/mole. The difference between the Wilcox and Huggins' value and the activation energy derived in this study could possibly be due to a difference in either the hydrogen or oxygen concentrations used in these two studies. The present nominal oxygen concentration was about half that of the Wilcox and Huggins value.

A second trend appearing in the data of Fig. 17 concerns the tendency of the data to shift toward longer aging times and higher aging temperatures as the hydrogen content of the specimens is increased. This would seem to imply that whatever interaction is occurring between the hydrogen and oxygen acts to decrease the kinetics of the pinning process. At this point, it would appear that the interaction effect not only results in a lower activation energy, but also that it slows the pinning action. This latter is not an unreasonable effect in lieu of the results that we have obtained with nickel specimens, where aging involved carbon-vacancy interactions. Very slow kinetics were observed in this case. The present data is not complete enough to allow, at this time, serious speculation as to the mechanism of the hydrogen-oxygen interaction.

Additional tests were made on groups of specimens charged for 3.0, 4.0 and 5.0 minutes, representing approximately 11, 14 and 17 wt ppm of hydrogen. With these specimens, it was found that, after removing the initial yield point during the 4% prestrain, it was not possible to age a yield point back into these specimens while using a testing temperature of 277 K. However, by lowering the testing temperature to 193 K, it again became possible to produce a yield point by aging in the temperature range from 480 to 495 K. Attempts were made
to determine the activation energy for the yield point return in these specimens, but were unsuccessful due to hydrogen loss from the specimens at these higher aging temperatures. However, limited results did show that, as before, increasing the hydrogen content above 8 wt ppm continued to decrease the pinning kinetics.

THE COMBINED EFFECT OF OXYGEN AND HYDROGEN ON THE STRESS-STRAIN BEHAVIOR OF NIOBIUM

It has been known for some time that the introduction of hydrogen into the niobium lattice alters the mechanical properties of the base material. Ravi and Gibala have studied the mechanical and thermodynamic effects of hydrogen on niobium single crystals; however, it appears that similar work on polycrystalline niobium has not been attempted.

An investigation has begun into the effects of hydrogen on the stress-strain behavior of niobium. The mechanical properties of hydrogenated niobium specimens were examined at 277 and 193 K. Figs. 18 and 19 show the fracture surface of a hydrogen-free niobium specimen and a niobium specimen containing 8 wt ppm of hydrogen, both tested at 277 K. It can be noted in these figures that, although the addition of a small amount of hydrogen is sufficient to produce a distinct fracture surface, at this temperature the fracture is ductile, occurring totally by microvoid coalescence. This can be compared with Fig. 20, which is a scanning electron micrograph of the fracture surface of a niobium specimen containing 8 wt ppm hydrogen, and tested at 193 K. This fracture appears to occur totally by a quasi-cleavage mode of failure characteristic of the slow
Fig. 18. Fracture surface of an unchanged MARZ grade niobium specimen deformed at $\dot{\varepsilon}=15 \times 10^{-4}$ and 277 K. Magnification 70X.

Fig. 19. Fracture surfaces of a MARZ grade specimen charged with 8 ppm hydrogen. Deformed at $\dot{\varepsilon}=1.6 \times 10^{-4}$ and 277 K. Magnification 64X.
Fig. 20. Fracture surface of a MARZ grade specimen with 8 ppm hydrogen deformed at 193 K. $\dot{\varepsilon}=1.6\times10^{-4}$. Magnification 120X.
strain-rate embrittlement phenomenon observed in niobium. It is possible, however, that the hydrogen alone is not responsible for the appearance of microvoid coalescence, or the quasi-cleavage mode which appears at lower temperatures. Grossbeck and Birnbaum have run tests on a niobium coarse grained polycrystalline specimen containing 5.5 a/o hydrogen, but a very low oxygen concentration, at 297 K, and obtained a fracture morphology roughly equivalent to that of Fig. 18. Longson has also observed that oxygen in niobium increases the susceptibility to hydrogen embrittlement. It would appear then that the loss in reduction in area and the change in fracture mode with test temperature could be due to an oxygen-hydrogen interaction which deserves more study.

An empirical analysis was performed on the stress-strain data of hydrogen-free niobium, niobium containing 8 wt ppm of hydrogen, and niobium containing 14 wt ppm of hydrogen in order to reveal the presence of the deformation stages. The formulation used for this analysis was the Crussard and Jaoul method applied to the modified Swift equation, 

\[ e = \varepsilon_0 + c \sigma^m, \]

where \( e \) is the true plastic strain, \( \sigma \) is the true stress, and \( \varepsilon_0, c \) and \( m \) are constants evaluated for each deformation stage from a \( \log \frac{\partial \sigma}{\partial e} \) vs. \( \log \sigma \) plot. Fig. 21 shows this plot for the hydrogenated and the hydrogen-free niobium stress-strain data at a test temperature of 277 K. This plot indicates that the hydrogen-free niobium has a two stage behavior at this temperature and strain-rate, characterized by \( m \) parameters of 2.90 and 3.22 for Stages II and III, respectively. (The Stage behavior of this material as a function of temperature has
Fig. 21. These modified Crussard and Jaoul plots show the effect of hydrogen on the deformation stage behavior.
been examined over the range of 293 to 945 K. These values of \( m \), at 277 K, are consistent with this earlier study.) The addition of hydrogen appears to have the effect of introducing an intermediate stage into the established stage structure. This intermediate stage appears between 4.5 and 14% true strain in both hydrogen concentrations tested, and has an \( m \) value of 2.49 and 1.70 for specimens containing 8 and 14 wt ppm, respectively. The data also indicates the possibility that a stage is developed in the microstrain region between 1 and 2% strain. The last point to be noted in Fig. 21 is that the addition of hydrogen has a minimal effect on the \( m \) parameters of Stages II and III, further emphasizing that the effect of hydrogen on the stage behavior of niobium, at this temperature and strain-rate, appears to be confined to discrete strain regions.

A significant observation from the dissertation work of Donoso has to do with the effect of static strain-aging, in the temperature interval from 600 to 630 K, on the work hardening rate during reloading. This effect is shown in Fig. 22, taken from Donoso's dissertation. The figure in question shows a plot of the increase in flow stress, within the strain interval from 0.02 to 0.05 strain, as a function of the aging time. This stress difference is a measure of the amount of work hardening obtained on reloading. Note that 

\[ \sigma_{0.05} - \sigma_{0.02} \]

is independent of the aging time, for all of the aging temperatures employed, up to a period of about \( 5 \times 10^3 \) secs. After this aging time, the data obtained from the 630 K specimens show a sharp increase in the average work hardening parameter with increasing time of aging. A similar effect is visible in the 600 K data beginning at about \( 2 \times 10^4 \) seconds. The interesting feature is that the 630 K curve shows that aging to about \( 10^5 \) seconds produced a 40% increase in work hardening. This is nearly equivalent to the increase in work hardening observed at the dynamic strain aging work hardening peak. This latter appears at about 770 K (\( \dot{\varepsilon} = 10^{-4} \) s\(^{-1}\)). We believe that it is significant that a single static aging treatment at 630 K can so alter the work hardening behavior on reloading. In other words, the static treatment in question completely alters the subsequent dynamic stress-strain behavior.

As a result of the above considerations, a study utilizing the electron
microscope was undertaken in order to attempt to relate the behavior of the
dislocation structure to observed changes in work hardening, as indicated in
Fig. 22. For this purpose, the following specimens deformed at 630 K were selected.
The first was a specimen that was strained directly to 0.055 strain. This speci-
men was chosen to show the structure that would develop in the absence of a
static strain-aging cycle. The TEM photograph of the specimen is shown in
Fig. 23. The second specimen was unloaded after a 0.02 prestrain to a small
holding stress of 10 MPa, and aged for 4000 secs. It was then reloaded and
strained to 0.055 strain. As may be seen in Fig. 22, this specimen was aged
to a time just short of that needed at 630 K to cause a rapid rise in the work
hardening rate. The third specimen was aged for 5.5 x 10⁴ sec. This aging pe-
cordence to a significant rise in the work hardening rate. The microstructures
of these specimens will be discussed shortly. First, however, the experimental
conditions employed in making these micrographs will be described.

The C.P. titanium samples which had been prestrained, aged and strained
were prepared for TEM by a standard window technique using foils which were
cut perpendicular to the tensile axis. In all grains examined, the basal plane
was nearly perpendicular to the plane of the foil. As a result, the basal plane
reflection was locatable with a minimum of tilting and all micrographs were
taken near the 0Tl0 pole. Each specimen was examined under three diffraction
conditions: (1) g = 0002; (2) g = 2T10; and, (3) g = 2T12. Although the criteria
for invisibility of defects is not strictly fulfilled by g • b = 0, the results
were sufficient to show that a dislocation network develops that contains only
a-type dislocations. This conclusion was arrived at by the absence of disloca-
tion structure when \( g = 2002 \) and \( g \cdot b = 0 \) for a-type dislocations. The other two orientations which yield \( g \cdot b = 0 \) for c and c+a type dislocations showed no such absence of dislocations, as can be seen by Figs. 23, 24 and 25.

**COMMENTS ON THE MICROSTRUCTURES**

The microstructures in Figs. 23, 24 and 25 show several interesting features. First, consider Figs. 23 and 24 corresponding to a specimen strained directly to 0.055 strain without aging and to another aged at 0.02 strain for 4000 secs before restraining up to 0.055 strain. Both specimens gave the same rise in flow stress between 0.02 and 0.55 strain. In other words, the work hardening in the two cases was equivalent. Both micrographs show dislocation networks with approximately equivalent mesh sizes. The directly strained specimen seems to differ from the aged specimen only in that there is a greater variation in the loop size of its mesh and that there are more dislocation segments parallel to the basal plane trace in this specimen. In both photographs, the basal plane trace direction is noted by a black line drawn across the photographs.

A decided change in the dislocation structure is visible in Fig. 25, corresponding to the specimen aged for 55,000 secs at 0.02 strain and then restrained to 0.055 strain. In this case, the mesh size is smaller and many segments are aligned essentially normal to the basal plane or parallel to the traces.
of the prism planes.

The data concerning the dislocation structures are limited at this point and represent only preliminary observations. Additional micrographs and other foils cut from longitudinal sections should give information about the three-dimensional character of the dislocation network. It is felt that this information is needed before worthwhile speculations about the nature of the hardening process can be made.

**OBSERVATIONS CONCERNING THE USE OF KIKUCHI MAPS AND LINES IN ANALYZING HCP MICROSTRUCTURE**

It has been often noted that in heavier metals and even in titanium which has undergone slight deformation, that the Kikuchi patterns which accompany the standard diffraction patterns are difficult to see. The result is increased difficulty in foil orientation determination and in specimen tilting technique.

The current work has been aided by two developments: (1) a detailed Kikuchi map of the region 90° away from the basal plane was generated by computer program; and, (2) a highly convergent beam technique was developed to produce clear and bright Kikuchi lines.

**Computer Generated Kikuchi Map**

The computer program generated and labeled individual diffraction patterns. These patterns were then traced, and Kikuchi lines drawn as perpendicular bisectors of the lowest order of \( g \) vectors. The tracings were reduced in size 70% and matched together to form the map. This map of the region 90° away from the basal plane is of considerable assistance in analyzing HCP diffraction patterns.
The computer program consisted of simply generating all possible values of \( \vec{g} \) from \( \overline{9909} \) to 9909 and determining if \( g \cdot r = 0 \) (\( r \) = beam direction or zone axis). Forbidden spots were labeled as such and determination of whether double diffraction could occur to give rise to forbidden reflectors was done manually during the tracing with possible forbidden reflections marked. Impossible forbidden reflections were not traced.

The first \( g \) for which \( g \cdot r = 0 \) was normalized to establish the \( x \) axis and a simultaneous solution of \( g_1 \cdot g_2 = 0 \), \( g_2 \cdot r = 0 \) and \( v + v + t = 0 \) for the zone indices gave a normalized vector \( g_2 \) for the \( y \) axis. The direction cosines were then established for each of the \( g \)'s which were in the pattern \( (g \cdot r = 0) \) and the results were plotted.

The actual map generated and drawn was approximately 3 feet by 4 feet and is, thus, too large to be included in this report.

**Observation of Kikuchi Lines**

The second aid in foil orientation was the use of a highly convergent beam to produce clear, bright Kikuchi lines. It was discovered that this could be accomplished on the Philips 301B by turning off the \( C_2 \) lens while in the diffraction mode. The accuracy of the observed pattern has been documented by Hren and Arey.

The results of this method can be seen in Fig. 26, which is an electron micrograph of the Kikuchi pattern of the 1540 pole. The observed Kikuchi lines are both clear and bright with the basal plane reflection being easily identified.
Fig. 22. The time-temperature dependence of the parameter $\sigma_{0.05} - \sigma_{0.02}$ evaluated after aging.
Fig. 23. Transmission electron micrograph of a specimen deformed at 630 K directly to a strain of 0.055. Foil section normal to tensile stress axis $\varepsilon=3.3\times10^{-4}$. Magnification 27,000X.

Fig. 24. TEM photograph of a specimen pretrained to 0.02 strain, aged for 4000 secs and then restrained to 0.055 strain. Foil section normal to tensile stress axis $\varepsilon=3.3\times10^{-4}$. Magnification 27,000X.
Fig. 25. TEM photograph of a specimen pre-strained to 0.02, aged for 55,000 secs and then restrained to 0.055 strain. Foil section normal to tensile stress axis $\varepsilon=3.3 \times 10^{-4}$. Magnification 27,000X.

Fig. 26. Kikuchi pattern for the 1540 zone as obtained with a commercial purity titanium specimen.
References

58. C. S. Hartley, Department of Materials Science and Engineering, University of Florida, 32611, private communication.