DEFORMATION PROCESSES IN REFRACTORY METALS

Progress Report

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PROGRESS REPORT

ABSTRACT

In the period covered by this report five papers will have been published. Abstracts of these papers are given in Sections 1 through 5 below. Three other papers have been submitted for publication. These are reproduced in their entirety in Appendices I through III. Appendix IV consists of a reproduction of a scientific report to ERDA dealing with the relationship of dynamic strain aging to slow strain-rate embrittlement.

Other work currently underway is discussed in Section 6 through 9. This includes a report of our yield point return studies on alloys of niobium containing both oxygen and hydrogen (Section 6). Here it has been observed that hydrogen has a complex effect on both the kinetics and energetics of the oxygen yield point return in niobium.

Section 7 describes our continuing work into the area of slow strain-rate embrittlement of oxygen by niobium and its relation to dynamic strain-aging.

Section 8 is an abstract of the data that has been obtained for the diffusion of oxygen and nitrogen in tantalum. These data are completed and will be prepared for publication shortly. They compliment similar data already published on the diffusion of oxygen and nitrogen in both niobium and vanadium.

Section 9 is a report of the preliminary work of a study of the effects of hydrogen on both slow strain-rate embrittlement and dynamic strain aging in vanadium. Both tension and compression tests are being carried out in this program. Because the embrittling effect of hydrogen can seriously reduce the tensile ductility it is not possible to study most aspects of dynamic strain aging using tension tests. Compression tests on the other hand do not suffer from this problem.

Section 10 is concerned with the work proposed last year based on a TEM study of strain-aged titanium specimens.

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 mechanisms, 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 Snoek 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 equi-
librium 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.

3. F.J.M. Boratto, A.M. Garde and R.E. Reed-Hill, Discussion
of "On the Calculation of the Tensile Strain Associated with

4. F.J.M. Boratto and R.E. Reed-Hill, "On the Calculations
of the Diffusion Coefficients of Oxygen and Nitrogen in Niobium,"

The Snoek peaks for oxygen and nitrogen in niobium have been remeasured
using a torsion pendulum equipped with LVDT transducers connected to an
oscillograph for automatic data recording. The peak temperatures were deter-
mined using a new numerical analysis of the peak shape. These new low temper-
ature data have been combined with high temperature direct data and intermediate
temperature high frequency internal friction data reported in the literature.
When it is assumed that the oxygen and nitrogen occupied octahedral positions
in the niobium matrix, the diffusion coefficients for both oxygen and nitrogen
atoms follow a simple Arrhenius behavior. In the temperature range of this
analysis (140 - 1000°C for oxygen and 270 - 1800°C for nitrogen) the equations
$D = (5.3E-7)\exp\left(-\frac{1.095E5}{RT}\right)$ and $D = (2.6E-6)\exp\left(-\frac{1.523E5}{RT}\right)$ apply for the diffusion
of oxygen and nitrogen, respectively. Entropy of activation calculations were
made using the above activation energies and frequency factors, and the results
agree well with reported values for other systems as well as with the theory
of Keyes. This good agreement suggests that the assumption that oxygen and
nitrogen prefer octahedral sites is probably correct.


The elastic after-effect technique offers a logical method for extending internal friction measurements to lower temperatures than are normally possible with the torsion pendulum. This technique becomes particularly powerful when strain-time relaxation curves are analyzed using a non-linear least square optimization method. Such a procedure is described in this note. As an example of its application, new data are presented that extend the range of measurement of the diffusion coefficient of oxygen in niobium to room temperature.
B. REPORT OF WORK IN PROGRESS

(6) THE INFLUENCE OF HYDROGEN ON THE OXYGEN YIELD POINT IN NIOBium

P.G. Watson and R.E. Reed-Hill

Experimental Procedure

In these experiments two grades of niobium were used, both supplied by the Materials Research Corporation as annealed 6.4 mm diameter rods. These consisted of a) high purity MARZ niobium and b) VP niobium of lower purity. The composition of both are given in Table I. Of primary interest to this investigation was the oxygen concentration, since at the aging temperatures which were employed, oxygen and hydrogen were the only interstitials with sufficient mobility to produce a yield point. The rods were machined into two different sized tensile specimens; the MARZ material into specimens of 3.2 mm diameter with a gage length of 13 mm and the VP material into specimens of 3.8 mm diameter and a gage length of 16.5 mm. All specimens were annealed under a dynamic vacuum of $10^{-5}$ TORR at 1373 K; the MARZ material for 30 minutes to produce a grain size of 100 microns and the VP material for 1 hour to produce a grain size of 26 microns.

The specimens were strained in an Instron TT-C tensile machine using a low temperature testing jig in baths of either ice and water or methanol cooled by liquid nitrogen. The high temperature aging was carried out in a Lauda NS-HT circulating bath which could be controlled to better than 1°K.

The testing procedure involved prestraining the specimen approximately 0.5% beyond the initial yield point, at a nominal strain rate of $6 \times 10^{-4}$ sec$^{-1}$, unloading the specimen and removing it from the testing machine and aging the specimen at a selected temperature for a given period of time. The specimen was then returned to the tensile machine and immediately reinserted.
in the low temperature bath. After a period of about 12 to 15 minutes, to bring the specimen to the testing temperature, the specimen was restrained plastically about 0.5% and the form of the yield point noted. This procedure was repeated at a single aging temperature, while varying the aging time, until the yield point matched the yield event chosen for these experiments. This event was the shortest aging time at which a noticeable yield drop could be observed.

Hydrogen was introduced into the tensile specimens by cathodic charging in a 10% $\text{H}_2\text{SO}_4$ solution. The hydrogen concentration was controlled by varying the time of charging and the cathodic current density. Each charging period was followed by a 48 hour holding period at room temperature, prior to tensile testing, to allow for hydrogen equilibrium within the specimen. After testing, a portion of the gage section from each specimen was removed and analyzed for its hydrogen concentration on a LECO, vacuum fusion hydrogen analyzer.

I. Data Analysis

The data was analyzed using the assumption that a critical number of thermally activated pinning sites, $n^*$, per unit length of dislocation line is required to produce the event chosen as indicative of the yield point reappearence. If the number of foreign atoms reaching the dislocation line, $n(t)$, obeys the Cottrell-Bilby formulation:

$$n(t) = an_o \left(\frac{ADt}{RT}\right)^{2/3} = an_o \left(\frac{AD}{RT}\right)^{2/3} \left\{\exp - \frac{Q}{RT}\right\}^{2/3}$$

where $n_o$ is the average concentration of foreign atoms, $a$ is a numerical factor, $A$ is an energy term and $D_o$ and $Q$ are the pre-exponential term and the activation energy in the diffusion equation of the solute atoms.

At $n(t) = n^*$

$$n^* = an_o \left(\frac{AD}{RT}\right)^{2/3} \left\{\exp - \frac{Q}{RT}\right\}^{2/3}$$

(1)
or re-arranging

\[
\left( \frac{n}{n_0} \right)^{3/2} \left( \frac{R}{AD_o} \right)^T_t = \exp\left( -\frac{Q}{RT} \right)
\]

(2)

taking the logarithm of both sides gives:

\[
\ln C + \ln \frac{T}{t} = -\frac{Q}{RT}
\]

(3)
or

\[
\ln \frac{T}{t} = -\ln C - \frac{Q}{RT}
\]

(4)

where C is a constant equal to the term in square brackets in Equation 2.

Thus, by plotting \( \ln \frac{T}{t} \) vs. \( \frac{1}{T} \) the activation energy for the process can be determined and, in principle, the responsible impurity atom identified by comparison with diffusion data.

**Experimental Results**

(a) MARZ Specimens Deformed at 273 K

The first series of experiments employed MARZ niobium tensile specimens with hydrogen concentrations ranging from <1 to 76 wt ppm strained at 273 K. The results are displayed in Fig. 1 and tabulated in Table II. Several features and trends can be noted in the data. The uncharged specimen displays an activation energy for the yield point return of 27.3 Kcal/mole. This value is in good agreement with the activation energy for the diffusion of oxygen in niobium (27.3 Kcal/mole\(^1\)), and indicates that in this regime the return of the yield point is due to the diffusion of oxygen.

Adding hydrogen to this material has two effects on the yield point reappearance. In the range of hydrogen contents from about 5-25 wt ppm the yield point return event occurs at longer times indicating a slowing of the process that was observed in the hydrogen free specimen, and the activation energy characterizing the process also drops to about 25 Kcal/mole. Upon
further hydrogen additions (up to 76 wt ppm) the process slows still further and the apparent activation energy drops to 10-20 Kcal/mole.

(b) VP Specimens Deformed at 273 K

Included in Fig. 1 are a hydrogen free VP niobium specimen and a hydrogen charged VP niobium specimen, both strained at 273 K. Line (10) in Fig. 1 represents data for uncharged VP niobium tested at 273 K. As can be seen from Table II the activation energy for this process is similar to that obtained from the hydrogen free MARZ niobium specimen at 273 K. The only difference is that the yield point returns more rapidly in the less pure specimen. This would be expected on the basis of Equation 1 since an increase of the impurity concentration $n_0$ should decrease the time required for a critical number of interstitials to reach the vicinity of the dislocation.

(c) VP Specimens Deformed at Various Temperatures

The second series of experiments investigated the variation of the activation energy for the yield point return process in hydrogen charged VP niobium specimens as a function of the testing temperature. Three different deformation temperatures were used. Figure 2 and Table III show the data obtained from the VP niobium specimens. At 296, 273 and 223 K, these specimens exhibited activation energies of approximately 24-26 Kcal/mole. Also, over this temperature range of 73 K, the kinetics of the yield point return did not shift significantly.

(d) MARZ Specimens Deformed Between 223 and 273 K

The third series of experiments examined hydrogen charged and uncharged MARZ niobium with the deformation temperature varied over the range of temperatures from 223 to 273 K. Several effects were evident. Specimens containing ~9 ppm of hydrogen exhibited an apparent activation energy that declined as the testing temperature was reduced from ~25 Kcal/mole at 273 K, to about 4 Kcal/mole at 233 K, where it appears to become constant (Figs. 3 and 4 and
Figure 1. Plot of the logarithm of the aging temperature divided by the aging time vs. the inverse of the aging temperature. Solid lines - MARZ niobium tensile specimens containing various amounts of hydrogen tested at 273 K and dashed lines - VP niobium tensile specimens tested at 273 K. MARZ niobium data line numbers 4 and 8 are not shown to avoid confusion since they lie over lines 2 and 3. The line numbers refer to Table II.
Figure 2. Plot of the logarithm of the aging temperature divided by the aging time vs. the inverse of the aging temperature for VP niobium containing various amounts of hydrogen. Tensile specimens strained at 296, 273 and 223 K. The line numbers refer to Table III.
Figure 3. Plot of the logarithm of the aging temperature divided by the aging time vs. the inverse of the aging temperature for MARZ niobium tensile specimens containing various amounts of hydrogen and strained at temperatures between 223 and 258 K. The line numbers refer to Table IV.
Figure 4. The apparent activation energy for the yield point return as a function of the straining temperature; MARZ niobium tensile specimen containing 9 wt ppm of hydrogen.

H. content ≈ 9 ppm
### TABLE I

#### Materials Selection

<table>
<thead>
<tr>
<th>Element</th>
<th>MARZ</th>
<th>VP</th>
</tr>
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<tbody>
<tr>
<td>O</td>
<td>&lt;10</td>
<td>50</td>
</tr>
<tr>
<td>H</td>
<td>&lt; 1</td>
<td>1</td>
</tr>
<tr>
<td>N</td>
<td>&lt; 1</td>
<td>15</td>
</tr>
<tr>
<td>C</td>
<td>&lt; 5</td>
<td>25</td>
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<tr>
<td>Fe</td>
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<td>Zr</td>
<td>---</td>
<td>50</td>
</tr>
<tr>
<td>Mo</td>
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<td>50</td>
</tr>
<tr>
<td>W</td>
<td>10</td>
<td>&lt;100</td>
</tr>
<tr>
<td>HF</td>
<td>---</td>
<td>100</td>
</tr>
<tr>
<td>Ta</td>
<td>100</td>
<td>500</td>
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### TABLE II

#### Hydrogen Activation Testing

<table>
<thead>
<tr>
<th>Specimens MARZ Nb</th>
<th>Hydrogen Concentration (wt ppm)</th>
<th>Activation Energy (Kcal/mole)</th>
<th>Testing Temperature (K)</th>
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<td>1</td>
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</tr>
<tr>
<td>2</td>
<td>7</td>
<td>24.1</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>8</td>
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</tr>
<tr>
<td>4</td>
<td>21</td>
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<td>25</td>
<td>24.0</td>
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<tr>
<td>6</td>
<td>41</td>
<td>16.8</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>46</td>
<td>10.6</td>
<td>273</td>
</tr>
<tr>
<td>8</td>
<td>68</td>
<td>26.1</td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>73</td>
<td>19.0</td>
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<table>
<thead>
<tr>
<th>VP Nb</th>
<th>Hydrogen Concentration (wt ppm)</th>
<th>Activation Energy (Kcal/mole)</th>
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<tr>
<td>10</td>
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<td>28.3</td>
</tr>
<tr>
<td>11</td>
<td>33</td>
<td>24.6</td>
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### TABLE III

<table>
<thead>
<tr>
<th>Specimens</th>
<th>Hydrogen Concentration (wt ppm)</th>
<th>Activation Energy (Kcal/mole)</th>
<th>Testing Temperature (K)</th>
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<tr>
<td>VP Nb</td>
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<td>24.5</td>
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<td>25.9</td>
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<td>7</td>
<td>26.0</td>
<td>223</td>
</tr>
<tr>
<td>17</td>
<td>16</td>
<td>25.3</td>
<td>223</td>
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### TABLE IV

<table>
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<tr>
<th>Specimens</th>
<th>Hydrogen Concentration (wt ppm)</th>
<th>Activation Energy (Kcal/mole)</th>
<th>Testing Temperature (K)</th>
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<tr>
<td>MARZ</td>
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<td>18</td>
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<td>223</td>
</tr>
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<td>19</td>
<td>9</td>
<td>4.3</td>
<td>233</td>
</tr>
<tr>
<td>20</td>
<td>9</td>
<td>4.4</td>
<td>228</td>
</tr>
<tr>
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<td>9</td>
<td>18.1</td>
<td>258</td>
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### TABLE V

<table>
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<th>Temperature (K)</th>
<th>(\tau_0) (sec)</th>
<th>(\tau_H) (sec)</th>
<th>(\tau_0/\tau_H) (sec)</th>
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<tr>
<td>453 K</td>
<td>300</td>
<td>(2 \times 10^{-12})</td>
<td>(1.5 \times 10^{14})</td>
</tr>
<tr>
<td>273 K</td>
<td>(6 \times 10^6)</td>
<td>(7 \times 10^{-11})</td>
<td>(8.6 \times 10^{16})</td>
</tr>
<tr>
<td>223 K</td>
<td>(3 \times 10^{11})</td>
<td>(2 \times 10^{-11})</td>
<td>(1.5 \times 10^{22})</td>
</tr>
</tbody>
</table>
Table IV). In addition the kinetics of the yield point return process for these specimens, decreased as the testing temperature was reduced.

Finally, a <1 ppm hydrogen specimen was tested at 223 K. The resulting yield point return activation energy was ~8 Kcal/mole and, as before, the kinetics of the return process was much slower than for the corresponding specimen tested at 273 K.

Discussion of Results

The data, taken as a whole, indicates that both the energetics and kinetics of the oxygen yield point are highly sensitive to both the hydrogen concentration and to the testing temperature, the temperature at which the specimen is prestrained and restrained.

The data for the yield point return in the uncharged (<1 wt ppm H) materials tested at 273 K can be simply interpreted as indicative of pinning by oxygen-dislocation interaction. Activation energies for the return process are 27-28 Kcal/mole in both VP and MARZ grade niobium, which is close to the activation energy for diffusion of oxygen in the niobium lattice. In addition, the kinetics observed in this process are consistent with those observed by other investigators.2,3

Before discussing the effects of a hydrogen addition on the return of the yield point, two general predictions of interstitial trapping models should be noted. These models predict that, in the temperature range where trapping occurs, the apparent activation energy for diffusion of the interstitial will increase from $Q_D$ to $(Q_D + E_B)$, where $Q_D$ is the activation energy for diffusion and $E_B$ is the binding energy between the diffusing interstitial and the trapping site. They also predict that the kinetics of the diffusion process will become slower as the concentration of trapping sites is increased, and accelerate as the concentration of the interstitial responsible for the aging is increased.
These models, however, include an assumption which limits their applicability to this series of tests. Namely that the base metal lattice contains trapping sites which are immobile. As can be seen in Table V this condition is not fulfilled in the temperature range of these experiments, if hydrogen is considered as a trap for oxygen. This table gives values for the mean time of stay of an oxygen atom $\tau_0$ and a hydrogen atom $\tau_H$ at a typical aging temperature, 453 K and at two of the deformation temperatures 273 and 223 K. Note that at all temperatures the hydrogen mobility is extremely high.

In the tests of hydrogen charged MARZ niobium at 273 K both the activation energy and the kinetics of the yield point return process appear to decrease monotonically with increasing hydrogen concentration (Table II). It can be seen that the first additions of hydrogen lowers the activation energy for the process to about 24-25 Kcal/mole. Thus, if it is assumed that these small additions (<25 w. ppm) do not significantly alter the basic mechanisms responsible for the yield point, then even at H:O ratios as high as 40, oxygen still remains the dominant pinning unit. Further, the primary effect of the hydrogen is to obstruct, to some extent, the diffusion of oxygen in the lattice resulting in a slowing of the kinetics of the yield point return process. The lowering of the activation energy is more difficult to understand. As was mentioned above, this effect is contrary to that predicted by models of interstitial trapping. This anomalous behavior is probably due to the limitations in the theory noted above relative to mobile trapping sites.

In the next year, internal friction techniques will be employed on hydrogen charged specimens in an effort to throw further light on this mechanism. The plan is to observe the oxygen Snoek peak, in the temperature range from 423 to 473 K, as a function of hydrogen content, using computer curve-fitting techniques and theoretical internal friction formulations to delineate the interactions of the several possible cooperating mechanisms.
Above hydrogen contents of about 40 wt ppm (H/O = 64) the kinetics in MARZ niobium continue to decrease along with the activation energies. In this range, up to about 70 wt ppm (H/O = 110) an ill-defined region of activation energies, between 10 and 18 Kcal/mole occurs. Activation energy values do not appear to be generally monotonic with hydrogen concentration possibly due to small variations in oxygen concentration occurring during each grain size anneal. In addition a low H/O ratio (high oxygen contamination) could be the cause of the high activation energy (26.1 Kcal/mole) which occurred in specimen 8 containing ~68 wt ppm of hydrogen. The effect of oxygen on these phenomena is discussed later in this section. It is likely that all of these activation energies, other than for specimen 7 (Q = 10.6 Kcal/mole) fall in a transition region involving the operation of two separate mechanisms. First, an oxygen dominated mechanism operating at low hydrogen concentrations, and second an oxygen-hydrogen mechanism operating at higher hydrogen concentrations. The second case is likely that observed by Wilcox and Huggins in their earlier yield point return (Q = 10.7 Kcal/mole) and dynamic modulus (Q = 8.5 Kcal/mole) experiments.5

The four MARZ niobium specimens containing 1 and 9 wt ppm of hydrogen and strained at temperatures from 258 to 223 K resulted in activation energies much lower than were encountered in the tests on MARZ niobium strained at 273 K. Fig. 4 shows that for small hydrogen concentrations (H/O = 14) the apparent activation energy for the yield point return approaches the activation energy for the diffusion of hydrogen, indicating that, at these temperatures, hydrogen has likely become the specie of importance in the yield point process. The constant activation energy obtained by testing at 228 and 233 K is possibly indicative of a distinct yield point formation mechanism involving hydrogen-dislocation interactions, where the hydrogen may exist in a cluster or complex in order to account for the observed pinning strength.
In contrast to this, the VP niobium strained at 223 K showed no significant shift in kinetics or energetics from the other temperatures displayed in Fig. 2. Activation energies for up to 16 wt ppm of hydrogen remain near 25 kcal/mole indicating that at 223 K the oxygen dominated mechanism is still operating. This emphasizes that the H/O ratio, rather than the hydrogen concentration, determines the operative mechanism at a given straining temperature.

In summation, it has been shown that the yield point process in niobium containing small amounts of oxygen and hydrogen is a complex process probably involving several distinct mechanisms, each dominant in a given deformation temperature range. Further contributions to the understanding of these mechanisms will be attempted through the use of internal friction techniques measurements.
THE RELATION BETWEEN STRAIN-AGING AND SLOW STRAIN-RATE EMBRITTLEMENT IN NIOBium-OXYGEN ALLOYS

P.G. Watson and R.E. Reed-Hill

The investigation of the relation between strain-aging and slow strain-rate embrittlement in niobium doped with oxygen has been started. It was found in earlier work that oxygen can have a catastrophic embrittling effect on niobium in the temperature range from 500 to 900 K. Within this temperature range, characteristics of the phenomena include an enhancement of the embrittlement at slower strain-rates, a mixture of intergranular and transgranular cracking within the ductility minimum and an immediate return to a ductile fracture mode at temperatures above and below the ductility minimum. Most of these characteristics are similar to those observed in the slow strain-rate embrittlement of niobium due to hydrogen which has been well investigated.

The present set of experiments are designed to obtain more extensive and more reproducible data in order to test for correlations between the slow strain-rate embrittlement phenomena and dynamic strain-aging. The earlier experimental procedures will be optimized in two major respects to increase the accuracy of the resulting data. These alterations involve increasing the size of the tensile test specimens and changing the procedures by which oxygen is introduced into the specimen.

The new and old tensile specimens are compared in Figs. 5 and 6, and below

<table>
<thead>
<tr>
<th>old specimen</th>
<th>new specimen</th>
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<tbody>
<tr>
<td>gage length: 5.0 mm</td>
<td>gage length: 6.9 mm</td>
</tr>
<tr>
<td>diameter: 0.5 mm</td>
<td>diameter: 1.7 mm</td>
</tr>
</tbody>
</table>

This new specimen with its larger cross-sectional area will reduce the
Figure 5. Niobium tensile specimen used in the work carried out in 1975 compared with a metric ruler with divisions in mm. This specimen has an acid etched gage section.

Figure 6. Machined niobium tensile specimen proposed for the dynamic strain-aging vs. oxygen embrittlement study displayed against a ruler with division in mm.
error in reading the stress due to frictional losses in the high temperature furnace capsule. It will also have a machined gage section, whereas the gage section for the old specimen was formed by etching. This should markedly improve the reproducibility of the data.

A new method of introducing oxygen into the tensile specimens in being employed in these investigations. The procedure involves placing 3.2 mm diameter, 38 mm long VP niobium rods in a 17 mm diameter niobium tube containing Nb$_2$O$_5$ powder. The tube ends are welded shut and the packet is placed in a tube furnace under an inert atmosphere at $\sim$1100 K. Oxygen pick-up is controlled by varying the soaking time at temperature. The rods are then removed from the packet and heated at $\sim$2000 K under a dynamic vacuum of $10^{-5}$ TORR for 60 minutes to eliminate the surface to center oxygen gradient resulting from the oxidizing anneal.

It has been observed that it is possible to obtain up to 1.75 wt % oxygen in a single oxidizing cycle involving heating in the oxide for 8 hours at 1130 K followed by a homogenization anneal at 2000 K for 60 minutes. It should be noted that true embrittlement of niobium by oxygen only begins to occur, at nominal strain-rates, at oxygen concentrations in excess of about 0.85 at. % and a well defined region of low ductility appears at about 2.3 at. %. Accordingly, this oxygen doping procedure should provide the range of oxygen concentrations required for this investigation by appropriately varying the length of the oxygen anneal. This doping procedure was proposed by F.N. Rhines. It has the advantage, since the specimen is only exposed to the partial pressure of oxygen in equilibrium with its oxide, of adding oxygen to the specimen without the formation of a surface scale. It appears to have considerable promise.

In last year's proposal it was indicated that Donoso's data would be examined for evidence of dynamic strain aging. This has been done and is
included as part of Appendix IV, ERDA Scientific Report, "Slow Strain-Rate Embrittlement and Its Relation to Strain-Age in Refractory Metals," pp. 9-11. The significant new observation relates to the work hardening peak as shown in Figs. 10 and 11 of the report. The temperature range of this peak runs from about 400 to 1000 K. As may be seen in Fig. 7 of the report this temperature range correlates well with the temperature range of the ductility minimum.

A planned part of this study is the use of tests in which specimens are to be aged under a constant load. During the past year an electronic switching device was designed which will maintain a tensile specimen under a constant load in an Instron machine. A prototype model was constructed and tested and the final model is now being installed in our TT-C Instron. This device is capable of maintaining a fixed load of from 1 to 1000 lbs. within the limits of ± 1 lb.
Elastic after-effect and internal friction experiments were performed on a standard Ké type torsion pendulum using tantalum specimens. Through computer optimization of the elastic after-effect curves and the internal friction spectrum curves the diffusion coefficients for oxygen and nitrogen in tantalum have been obtained over a wide range of temperatures.

These data when combined with high temperature data reported in the literature yield:

\[ D = (1.0497 \times 10^{-6}) \exp(-\frac{1.1043 \times 10^5 \text{ J/mole}}{RT}) \text{ m}^2/\text{s} \]

\[ D = (5.2124 \times 10^{-7}) \exp(-\frac{1.5848 \times 10^5 \text{ J/mole}}{RT}) \text{ m}^2/\text{s} \]

for the oxygen and nitrogen diffusivities, respectively.

The high temperature data points agreed well with low temperature results when an octahedral occupancy was assumed for both oxygen and nitrogen.
(9) A COMPARISON OF DYNAMIC STRAIN AGING AND SLOW STRAIN-RATE EMBRITTLEMENT IN HYDROGENATED VANADIUM

L.P. Beckerman and R.E. Reed-Hill

Interstitial solutes are known to cause both dynamic strain aging and slow strain-rate embrittlement phenomena in transition metals. Since diffusion of the solute has been found to be rate controlling in both classes of phenomena, it is reasonable to assume there may be further interrelations.

While significant studies of hydrogen induced slow strain-rate embrittlement in transition metals have been completed, very little work has been done to study the effect of hydrogen on dynamic strain aging in these metals. A study of the phenomena associated with dynamic strain aging, such as serrated plastic flow, abnormal work hardening rates and an abnormally low strain-rate sensitivity, require that a significant portion of the stress-strain curve be obtainable at strains beyond the yield point. Since the majority of investigations that have been made have utilized tensile tests and since failure occurs catastrophically at or near the yield point, within the embrittlement temperature range, very little data has been obtained that could be used to study dynamic strain aging.

The object of this initial study has been to investigate the feasibility of utilizing compression tests to study both slow strain-rate embrittlement and dynamic strain aging in vanadium containing dissolved hydrogen. The catastrophic failure associated with necking of tensile specimens is eliminated by the use of the compression test and significant portions of the plastic region of the stress-strain curves have been obtained. While Chen and Arsenault have investigated vanadium single crystals tested in compression, a comprehensive study using polycrystalline specimens has not been made.
Experimental Procedures

MARZ grade vanadium 99.9995% pure in the form of 6.35 mm diameter rod was obtained from the Materials Research Corporation. According to the manufacturer it contained in wt ppm: C-20, O-60, H<-1 and N-15.

Cylindrical tensile specimens were machined having a gage length of 25 mm and a gage section diameter of 3.8 mm. In addition 70 mm lengths of the rod were cut as stock for compression specimens and these along with the tensile specimens were annealed in a dynamic vacuum of $10^{-5}$ TORR at 1100°C for one hour to yield a uniform grain size of 50 μm.

Hydrogen was introduced into the tensile specimens and the 70 mm long rods by cathodic charging in a 12.5% solution of sulfuric acid at a current density of 13.7 A/cm$^2$ for 3 minutes. The tensile specimens and rods were allowed to homogenize at room temperature for a minimum of 3 days. The 70 mm rods were then cut into compression specimens with a height of 16 mm and a diameter of 6.35 mm giving a height to width ratio of 2.5. Analyses made on a LECO hydrogen analyzer yielded hydrogen concentrations in the charged specimens of 127 ± 12 ppm and in the uncharged specimens of 1.4 - 1.7 ppm. All analyses were made immediately after testing.

Tension and compression tests were conducted on an Instron at four temperatures: 298, 273, 178 and 77 K. A liquid nitrogen bath was used for the 77 K tests, melting methanol for the 178 K tests and melting ice for the 273 K tests. Tension tests were conducted at a nominal strain-rate of $6 \times 10^{-4}$/sec and compression tests at a nominal strain-rate of $5 \times 10^{-4}$/sec.

Experimental Results

A comparison of tension and compression tests of hydrogenated vanadium specimens is shown in Fig. 7. In this diagram engineering stress-strain data are shown for three temperatures: one above the embrittlemement temperature range,
Figure 7. Engineering stress-strain curves for hydrogenated vanadium specimens. (a) compression - 77 K, (b) tension - 77 K, (c) compression - 178 K, (d) tension - 178 K, (e) compression - 298 K and (f) tension - 298 K.
Necking begins in the room temperature tensile test at $\epsilon = 8.9\%$, in the 178 K test at $\epsilon = 0.5\%$ and in the 77 K test at $\epsilon = 6.3\%$. This clearly demonstrates that the data available from tensile tests, within the slow strain-rate embrittlement range, are insufficient to enable a comprehensive study of dynamic strain aging in this range. The advantage of compression testing is clearly seen since it is possible to obtain extended stress-strain curves in compression within the embrittlement temperature range. The specimens were loaded to the capacity of the compression rig without failure of the specimens occurring. This ability to obtain a complete stress-strain curve should make possible a study of the various dynamic strain aging phenomena.

The effect of hydrogen on the behavior of vanadium in compression at various temperatures is shown in Fig. 8. It can be seen that the effect of dissolving hydrogen interstitially in vanadium is to raise both the yield stress and the flow stress.

The yield stress is plotted against temperature in Fig. 9. The effect of hydrogen is to increase the yield stress by 21.4% at room temperature, by 9.2% at the liquid nitrogen temperature, and by 58.6% within the embrittlement temperature range.

The effect of hydrogen on the Swift equation parameter, $m$, for the compression tests at four test temperatures is shown in Fig. 10. The parameter $m$ is the exponent applied to the stress in the Swift equation

$$\epsilon = \epsilon_0 + C \sigma^m$$

It was also observed that there was no significant effect of hydrogen on the strain-rate sensitivity at 178 K. In addition serrations were not observed on any of the stress-strain curves that were obtained.
True stress vs. true strain compression curves. (a) hydrogenated - 77 K, (b) unhydrogenated - 77 K, (c) hydrogenated - 178 K, (d) unhydrogenated - 178 K, (e) hydrogenated - 273 K and (f) unhydrogenated - 273 K.
Figure 9. The variation of the yield point with temperature. (a) hydrogenated specimen and (b) unhydrogenated.
Figure 10. Plot of the Swift equation parameter m as a function of temperature for compression tests. (a) hydrogenated specimens and (b) unhydrogenated.
Discussion

The results obtained in this study reflect the dependence of the mechanical behavior of vanadium on temperature and hydrogen content. The tensile tests conducted at 178 K showed the high yield stress and brittle failure expected within the embrittlement temperature range. The actual temperature at which the slow strain-rate embrittlement effect has been found by other investigators to be most dramatic, that is, where the ductility is at a minimum and the yield stress at a peak, depends not only on temperature but on strain-rate and hydrogen content. Eustice and Carlson\textsuperscript{11} report that for a hydrogen content held constant at 10 ppm, with a strain rate of $1.3 \times 10^{-4}$/sec, the ductility minimum occurs at $-105^\circ$C, whereas at a strain-rate of $8.3 \times 10^{-3}$, a difference of less than one order of magnitude, the ductility minimum occurs at $-80^\circ$C, a difference of 25°C. This same pattern of behavior was found by Chen and Arsenault\textsuperscript{10} for hydrogenated V single crystals.

Eustice and Carlson,\textsuperscript{11} Chen and Arsenault\textsuperscript{10} also found that changing the strain-rate changes the range of temperatures within which the embrittlement phenomena occur, the temperature at which the yield stress increases rapidly and the extent of the yield stress plateau.

The existence of a yield stress plateau and a minimum of the strain-rate sensitivity are phenomena observed during dynamic strain aging. While the existence of a yield stress plateau has been observed in hydrogenated vanadium very little work has been done to determine the dependence of strain-rate sensitivity on temperature. Chen and Arsenault\textsuperscript{10} tested hydrogenated and unhydrogenated V single crystals in compression, thus allowing them to obtain enough of the plastic portion of the stress-strain curve to run strain-rate sensitivity tests. They found the addition of H to V single crystals caused a minimum in SRS to occur at 153 K. It is interesting to note that at approximately 175 K very little difference in SRS was obtained between their hydrogenated and
unhydrogenated specimens, though at only 20 K below this temperature a marked
difference in the SRS was observed. Thus the SRS minimum due to hydrogen in
vanadium appears to be very narrow. This may account for the lack of a
difference in the SRS between the hydrogenated and unhydrogenated specimens
tested in this study at 178 K.

In general it appears that the extent to which the various slow strain-
rate embrittlement and dynamic strain aging phenomena are displayed in hydro-
genated vanadium depends on the combination of temperature and strain-rate
that are used.

This study generated results that are in good agreement with the results
of other investigators. It has, in addition, determined that it is feasible
to obtain data from compression tests of polycrystallines that would permit a
comprehensive study of dynamic strain aging phenomena. Testing at a series
of closely spaced temperatures and strain-rates is now required since the
effects to be studied may occur to a significant extent within a temperature
interval as short as 25 K at a particular strain-rate. In order to make tests
at arbitrary temperatures in the embrittlement range a suitable cryostat is
needed. This device is being designed and it is planned to construct it in
the coming year.
The work that had been proposed in last year's proposal concerned with a TEM study of strain-aged titanium specimens had to be discontinued. The effort that was to have been devoted to this part of the investigation was diverted to a study of strain-aging in vanadium due to hydrogen employing compression specimens. The results of this new work is described in Section 10 of this report.

The change in direction of part of the project was necessitated by the fact that Mr. Dennis Wise was called up prematurely by the U.S. Air Force to serve his ROTC commitment. This necessitated the hiring of a new graduate student assistant, Ms. Linda Beckerman, whose interests and training are more compatible with the vanadium investigation.
REFERENCES


Introduction

In a recent paper a new method for the analysis of elastic after-effect curves, through the use of a computer optimization technique, was presented. The method, when applied to relaxation curves of niobium, was shown to be able to yield relaxation times covering a range of five orders of magnitude. In the present work the same technique is applied to elastic after-effect curves of vanadium specimens in order to obtain new data on the diffusion coefficients of both oxygen and nitrogen in this metal.

Torsion pendulum experiments were also performed at two different vibration frequencies. The resultant internal friction spectra were analyzed with the help of a non-linear least square optimization technique in order to separate the data corresponding to the overlapping oxygen and nitrogen peaks in vanadium.

Experimental Methods and Results

The elastic after-effect and internal friction experiments were performed on a standard Kê type torsion pendulum previously described.

Marz grade vanadium specimens were purchased from the Materials Research Corporation in the form of thin annealed wires. The specimens, 80 mm long by 0.76 mm diameter, were surface cleaned in a solution of 1.5 parts HNO₃,
3 parts HF and 3 parts HCl prior to the experiments.

The elastic after-effect curves were analyzed by the non-linear least square optimization program assuming the equation:

$$\varepsilon = \varepsilon_m \exp\left(-\frac{t}{\tau}\right) + \varepsilon_o$$  \hspace{1cm} (1)

where $\tau$ is the relaxation time and $\varepsilon_m$ and $\varepsilon_o$ are constants. All three parameters $\varepsilon_o$, $\varepsilon_m$, and $\tau$ are optimized by the program.

Table I shows the results. The diffusivities were calculated from the relaxation times assuming octahedral site occupancy and the relation:

$$D = \frac{4}{30\pi}$$

$$D = \frac{2}{30\pi}$$

\hspace{1cm} (2)

<table>
<thead>
<tr>
<th>(\tau) (ns)</th>
<th>(D) (m^2/s)</th>
<th>(T) (^\circ\text{C})</th>
<th>(\ln D)</th>
<th>(1000/\tau) ((^\circ\text{K})^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oxygen</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>12.6</td>
<td>2.023E-22</td>
<td>132.8</td>
<td>-49.952</td>
<td>2.463</td>
</tr>
<tr>
<td>30.3</td>
<td>8.411E-23</td>
<td>123.5</td>
<td>-50.830</td>
<td>2.521</td>
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<td>39.6</td>
<td>6.436E-23</td>
<td>120.5</td>
<td>-51.098</td>
<td>2.540</td>
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<td>49.1</td>
<td>5.191E-23</td>
<td>117.8</td>
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</tr>
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<td>112.0</td>
<td>-51.700</td>
<td>2.596</td>
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<td>107.1</td>
<td>2.380E-23</td>
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<td>2.622</td>
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<td>217.1</td>
<td>1.174E-23</td>
<td>100.8</td>
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<td>2.674</td>
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<td>376.9</td>
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<td>876.6</td>
<td>3.007E-24</td>
<td>88.5</td>
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<td>1333.0</td>
<td>1.912E-24</td>
<td>84.8</td>
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<td>2.793</td>
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<td>Nitrogen</td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6.9</td>
<td>3.694E-22</td>
<td>216.3</td>
<td>-49.350</td>
<td>2.043</td>
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<td>12.0</td>
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<td>209.5</td>
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<td>2.072</td>
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<td>203.0</td>
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<td>2.100</td>
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<tr>
<td>37.1</td>
<td>6.869E-23</td>
<td>195.5</td>
<td>-51.032</td>
<td>2.134</td>
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<td>51.1</td>
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<td>-51.353</td>
<td>2.163</td>
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<td>89.9</td>
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<td>-52.814</td>
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<tr>
<td>396.4</td>
<td>6.429E-24</td>
<td>167.0</td>
<td>-53.401</td>
<td>2.272</td>
</tr>
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</table>
The internal friction spectra were analyzed assuming the equation:

\[ d = d_m^o \text{sech}\left(\frac{Q_s^o}{RT}\right) + d_m^n \text{sech}\left(\frac{Q_s^n}{RT}\right) \]

where \( d \) is the logarithmic decrement, \( T_p \) the Snoek peak temperature, \( Q_s \) the "shape analysis activation energy" and \( d_m \) the log-decrement at \( T_p \). The superscripts \( o \) and \( n \) refer to the oxygen and nitrogen Snoek peaks, respectively. The six parameters in Eq. 3, \( d_m^o, Q_s^o, T_p^o, d_m^n, Q_s^n, T_p^n \) were obtained by the use of the non-linear least square optimization program. Table II summarizes all the results that were obtained.

**TABLE II**

Equation (3) Parameters Obtained After Non-Linear Least Square Optimization of Internal Friction Spectra of Vanadium

<table>
<thead>
<tr>
<th>Nominal Frequency</th>
<th>Interstitial Peak Freq. (Hz)</th>
<th>( Q_s ) (J/mole)</th>
<th>( d_m )</th>
<th>( T_p ) (°C)</th>
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<tr>
<td>0.50</td>
<td>oxygen</td>
<td>0.501</td>
<td>1.156E5</td>
<td>4.9E-3</td>
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<tr>
<td>0.50</td>
<td>nitrogen</td>
<td>0.500</td>
<td>1.531E5</td>
<td>7.5E-3</td>
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<td>0.81</td>
<td>oxygen</td>
<td>0.819</td>
<td>1.128E5</td>
<td>9.1E-3</td>
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<tr>
<td>0.81</td>
<td>nitrogen</td>
<td>0.816</td>
<td>1.352E5</td>
<td>6.6E-3</td>
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</tbody>
</table>

Figure 1 shows the data for the 0.81 Hz experiment. The solid curve is the theoretical equation using the parameters from Table II. The two decomposed Snoek peaks are also shown as dotted lines.

Tables III and IV show the internal friction results and the corresponding diffusion constants. Other values reported in the literature are also shown as well as the elevated temperature results of Schmidt and Warner.\(^3\)
### TABLE III

**Internal Friction Results**

<table>
<thead>
<tr>
<th>Freq. (Hz)</th>
<th>D (m²/s)</th>
<th>T (°C)</th>
<th>ln D</th>
<th>1000/T (°K)⁻¹</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Oxygen</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.378</td>
<td>6.053E-21</td>
<td>172.4</td>
<td>-46.553</td>
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<td>4</td>
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<td>0.501</td>
<td>8.023E-21</td>
<td>172.3</td>
<td>-46.272</td>
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<td>0.682</td>
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<td>0.819</td>
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<td>-45.781</td>
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<td>2.168</td>
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<td>1.72</td>
<td>2.754E-20</td>
<td>193.4</td>
<td>-45.039</td>
<td>2.143</td>
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<tr>
<td><strong>Nitrogen</strong></td>
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<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.350</td>
<td>5.605E-21</td>
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<td>0.500</td>
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<td>279.2</td>
<td>-45.123</td>
<td>1.810</td>
<td>4</td>
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</tbody>
</table>

### TABLE IV

**High Temperature Measurements.**

*After Schmidt and Warner*

<table>
<thead>
<tr>
<th>D (m²/s)</th>
<th>T (°C)</th>
<th>ln D</th>
<th>1000/T (°K)⁻¹</th>
</tr>
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<tbody>
<tr>
<td><strong>Oxygen</strong></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>2.5E-9</td>
<td>1825</td>
<td>-19.807</td>
<td>0.477</td>
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<tr>
<td>1.5E-9</td>
<td>1735</td>
<td>-20.318</td>
<td>0.498</td>
</tr>
<tr>
<td>1.0E-9</td>
<td>1650</td>
<td>-20.723</td>
<td>0.520</td>
</tr>
</tbody>
</table>

| **Nitrogen** |        |      |               |
| (0.8-0.91)E-9 | 1825 | -20.880 | 0.477         |
| (0.7-0.67)E-9 | 1735 | -21.102 | 0.498         |
| (0.35-0.35)E-9 | 1650 | -21.773 | 0.520         |

In Figs. 2 and 3 all the data points from Tables I, III and IV are plotted in an Arrhenius diagram. The best straight lines through all data points yield the following equations:
D = (5.021E-6) \exp\left(-\frac{1.5104E-5 \text{ J/mole}}{RT}\right) \text{ m}^2/\text{s} \quad (4)

and

D = (2.661E-6) \exp\left(-\frac{1.2471E5 \text{ J/mole}}{RT}\right) \text{ m}^2/\text{s} \quad (5)

for the nitrogen and oxygen diffusivities respectively. The errors associated with the above values when calculated based on one standard deviation are:

\[ \pm 3.7E-7 \] Do nitrogen
\[ \pm 2.7E-7 \] Do oxygen
\[ \pm 3.5E-2 \] Q nitrogen
\[ \pm 3.5E-2 \] Q oxygen

Powers and Doyle\(^6\) reported the values 0.92E-6 and 1.3E-6 m\(^2\)/s for the frequency factor of nitrogen and oxygen respectively when only mechanical relaxation tests were performed. Schmidt and Warner\(^7\) using a combination of their previous data\(^3\) with Powers and Doyle results reported values of 4.17E-6 and 2.46E-6 for the same constants. The smaller values obtained by Powers and Doyle are probably the result of a higher interstitial content in their specimens. The minimum value of \(d^\text{m}\) in Powers and Doyle paper was 18.8E-3 which is at least twice as high as the value shown in Table II. The value of \(d^\text{m}\) is not reported in their paper, but because of the ease of oxygen contamination in refractory metals\(^8\) it may be even higher than the value of \(d^\text{m}\).

High values of interstitial content result in an interaction between impurities which cause the average relaxation time to be higher than the relaxation time for a single process. This problem was recognized by Powers and Doyle themselves\(^6\) and similar effects were investigated in tantalum\(^8,9\) by those authors.
Acknowledgements

F.J.M. Boratto gratefully acknowledges the financial support provided by a fellowship from the Technological Center of Minas Gerais, CETEC, Brazil. The support of the experimental work and the contribution of R.E. Reed-Hill, which was made by the Energy Research and Development Administration under contract AT-(40-1)-3262, is also gratefully acknowledged.

References

Figure 3

Computer plot of the internal friction spectrum of vanadium. 
Solid curve according to Eq. [3] after non-linear least square optimization of the background subtracted data points.
Figure 2.

Arrhenius plot of the oxygen diffusion data in vanadium. Solid line according to Eq. [5].
Figure 3

Arrhenius plot of the nitrogen diffusion data in vanadium. Solid line according to Eq. [4].
APPENDIX II

Paper submitted to Metallurgical Transactions

STATIC STRAIN AGING DUE TO CARBON IN A FCC METAL,
NICKEL 200, DEVELOPMENT OF AN INITIAL YIELD POINT

W. R. Cribb* and R. E. Reed-Hill**

ABSTRACT

A model is proposed for the development of the first stage of the yield point return in Nickel 200. It is assumed that immediately after straining and unloading, vacancies created during deformation become trapped by interstitial carbon atoms. The carbon-vacancy pairs thus formed then reorient quickly in the stress field of nearby dislocations thus reducing the dislocation line energy so that dislocation pinning occurs. This model is an extension of that given by Rose and Glover in 1966 for austenitic stainless steel.

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**Department of Materials Science and Engineering, University of Florida, Gainesville, Florida 32611.
INTRODUCTION

In a previous paper, work on static strain aging in nickel containing carbon was reported. Tensile specimens of Nickel 200 were prestrained 5%, aged between 10 and $10^6$ seconds at temperatures between 373 and 473 K, and then they were restrained. The experimental observations were observed to support an aging mechanism originally proposed by Rose and Glover and by Jenkins and Smith for austenitic stainless steels. In this mechanism, the hardening agent is assumed to be a carbon-vacancy pair which re-orient in the stress field of a dislocation. The pair rotation is accomplished by the movement of the vacancy rather than the carbon atom since the vacancy has a lower activation energy for motion, about 0.87 eV (20.0 kcal/mole) compared to 1.43 eV (33.0 kcal/mole) for a carbon atom in nickel. Rose and Glover proposed a three-stage aging process: a) rotation of existing pairs; b) formation of new pairs; c) migration of vacancies into ordering regions around dislocations.

This paper concerns the first stage in the aging process during which vacancies created during deformation are trapped by interstitial carbon atoms and the resulting carbon-vacancy dipoles re-orient into their lowest energy configuration with respect to nearby dislocations. The result is an initial component of the yield point that forms very quickly.

The analogous process of ordering of the carbon atoms in iron in the stress field of a dislocation was examined by Shoeck and Seeger in 1959. Assuming the concentration of solute was small, they showed that the line energy of a dislocation surrounded by a Snoek ordered atmosphere was decreased by an amount $U_o$ given by
\[ U_0 = \frac{n_0 A^2}{kT} \ln \frac{3LkT}{A} \]  

where \( n_0 \) is the number of interstitials per unit volume, \( A \) an interaction constant, \( L \) a cutoff radius of the order of \( 10^{-4} \) cm which takes care of the cancellation of the stress field of neighboring dislocations, and \( kT \) the thermal energy.

They next showed that the increment of the applied stress, \( \Delta \tau \), necessary to pull the dislocation from the ordered atmosphere was given by

\[ \Delta \tau = \frac{U_0 kT}{?bA} \]

where \( b \) is the Burgers vector magnitude. The yield stress increment resulting from the ordering of solute atoms in the stress fields of dislocations has generally been ignored in static strain aging experiments probably because it occurs very quickly at the temperatures that are normally involved. Snoek ordering, however, could explain the rapid static strain aging phenomena observed in tensile tests on a low carbon steel by Wilson and Russell\(^5\) as well as similar observations on a range of materials (for example, Carpenter on tantalum-oxygen\(^6\) and niobium-oxygen\(^7\); Owen and Roberts\(^8\) on martensite; Rose and Glover\(^1\) on stainless steel). Support for this view also comes from the work by Nakada and Keh\(^9\) who observed rapid aging in iron-nitrogen single crystals.

The Quist and Carpenter\(^7\) investigation of dislocation pinning in Nb-O alloys between 273 and 313° K using a high frequency internal friction technique is
noteworthy. They observed that dislocation pinning was effectively completed in the period of about one oxygen atom jump time. This is consistent with a phenomenon based on the Snoek effect.

RESULTS AND DISCUSSION

The Distribution of Vacancies, Carbon Atoms and Dislocation After Plastic Deformation

The vacancy concentration in nickel has been estimated by Kressel and Brown\textsuperscript{10} to be given by the equation

$$c_v = 2.1 \times 10^{-4} \varepsilon$$  \hspace{1cm} (3)

A 5% prestrain accordingly generates an atom fraction of vacancies equal to about $10^{-5}$. The present Nickel 200 contains approximately 0.5 a/o carbon so that at 5% strain, the carbon-to-vacancy ratio should be approximately 500 to 1. From this it may be deduced that the mean carbon atom spacing was approximately 6b while the mean vacancy spacing was approximately 50b.

After 5% strain, the dislocation density\textsuperscript{11,12} is estimated to be between 2.5 and $8 \times 10^9$ cm\textsuperscript{-2}. Assuming an equidistant array of straight dislocation lines as a first approximation to the dislocation configuration, then their mean spacing should have been approximately 450 to 800b.

Vacancy Trapping by Carbon Atoms

Vacancies in a metal are attracted to oversized impurity atoms by a hydrostatic pressure gradient. The strain energy released when a vacancy moves from infinity to an impurity is known as the binding energy of the vacancy-impurity atom pair. The formation of a pair is commonly called trapping. It has been postulated that trapping of vacancies by carbon atoms in austenitic
stainless steel forestalls radiation-induced swelling or void formation in certain critical nuclear reactor parts.\textsuperscript{13} Trapping of carbon by vacancies in irradiated mild steel has been demonstrated.\textsuperscript{14}

The Concentration of Carbon-Vacancy Pairs

After deformation the vacancies created by the deformation should become trapped by carbon atoms within a very short period of time since the vacancies in Nickel 200 only have to travel a few atomic spacings in order to reach a carbon atom.

The apparent activation energy for the diffusion of a vacancy is sensitive to the presence of impurities. This is because trapping by the impurities tends to slow down the migrating vacancy.\textsuperscript{15,16} Thus, in pure nickel, the measured vacancy migration energy is between 0.8 (18.4) and 0.9 eV (20.7 kcal/mole) and for impure nickel\textsuperscript{16,17} (99.9\% pure with an unspecified amount of carbon), it is approximately 1.1 eV (25.3 kcal/mole). Thus, one may deduce an approximate binding energy of carbon atoms to vacancies of between 0.2 (4.6) and 0.3 eV (6.9 kcal/mole) on the assumption that the activation energy is approximately the sum of the trapping and diffusion energies. Assuming that dislocations do not affect the concentration and that equilibrium is established, the concentrations of single (free) vacancies ($c_v^f$) and vacancies bound in carbon-vacancy parts ($c_{cv}$) vary with the carbon concentration ($c_c$), temperature $T$, and the carbon-vacancy binding energy ($B$) according to the equations\textsuperscript{15}

$$c_{cv} = Z c_c^f c_v^f e^{B/kT}$$  \hspace{1cm} (4)

and

$$c_v = c_v^f + c_{cv}$$  \hspace{1cm} (5)
where $c_v$ is the vacancy concentration generated during plastic deformation, $c_c^f$ is the free carbon concentration, and $Z$ is 6, the nearest neighbor coordination number for a carbon atom in an fcc octahedral lattice site. For $c_c = 5 \times 10^{-3}$, $c_v = 10^{-5}$, assuming $B$ is 0.3 eV (6.9 kcal/mole) and at a temperature of 373 K, the carbon-vacancy pair concentration should be $9.97 \times 10^{-6}$, or very close to the total vacancy concentration of $10^{-5}$. The free vacancy concentration is then, from Equation 5, $3 \times 10^{-8}$ atom fraction. Thus, almost all (99.7%) vacancies should become trapped by carbon atoms. In spite of this fact, the number of free vacancies is still much greater than would be expected under equilibrium conditions. At 373 K, assuming a vacancy formation energy, $c_v^f$, of 1.7 eV (39 kcal/mole), the equilibrium vacancy concentration in the absence of carbon (and deformation) should be approximately $1.9 \times 10^{-23}$ atom fraction. This is about 15 orders of magnitude smaller than the above computed free vacancy concentration after deformation.

**Theory of Locking by Carbon-Vacancy Pairs**

Let us consider the locking of a screw dislocation in the fcc lattice by an ordered atmosphere of dipoles. The reasoning is analogous to that used by Schoeck and Seeger\(^4\) for carbon (or nitrogen) in alpha iron. However, the carbon-vacancy dipole defect in a fcc lattice is somewhat different from the carbon atom in a bcc metal. The carbon atom in nickel is assumed to occupy an octahedral site, e.g., the body-centered position of the fcc unit cell. Its six nearest neighbors are face-centered atoms. A dipole is formed when a vacancy is situated on one of these six face-centered positions. Since the carbon-vacancy dipole may be oriented along any of the three \(<100>\) directions, its orientation will be denoted by the orientation numbers 1, 2 or 3 corresponding to the \([100]\), \([010]\) and \([001]\) orientations, respectively. The screw dislocation
line may lie along any of the $<101>$ directions. For the purpose of this paper, the $[101]$ direction will be assumed. Each of the three carbon-vacancy dipole orientations will interact differently with this screw dislocation so that there are three interaction energies. If a carbon-vacancy dipole in the 1-orientation flips to orientation 2, the interaction energy between that particular carbon-vacancy pair and the dislocation is changed by $u_1 - u_2$ where $u_1$ and $u_2$ are the respective interaction energies of a type 1 dipole and a type 2 dipole. The energies of the three dipole orientations can be approximated following the procedure outlined by Barnett and Nix:

$$u_1 = -\frac{A}{r} (\sin \theta + \sqrt{2} \cos \theta) = u$$  \hspace{1cm} (6a)
$$u_2 = 0$$  \hspace{1cm} (6b)
$$u_3 = -u$$  \hspace{1cm} (6c)

where $A$ is an interaction constant assumed approximately equal to 0.2 eV·b ($4.6$ kcal·b/mole) and $r$ and $\theta$ are angular coordinates originating at the dislocation core. This can be rationalized as follows.

According to Barnett and Nix, the interaction energy for a $[001]$ defect is

$$u = -\frac{3}{\sqrt{3}} V e \frac{c_{44}}{4\pi r} (\sin \theta + \sqrt{2} \cos \theta)$$  \hspace{1cm} (7)

where $V = a^3/4$ (the atomic volume of a solvent atom). The value for $\Delta V$, the dilation, due to carbon in nickel can be deduced from the lattice parameter measurements of Ni-C alloys by Zwell et al.

Their result is

$$a(Å) = 3.5238 + 0.74 c_c$$  \hspace{1cm} (8)

where $a$ is the lattice parameter and $c_c$ the carbon concentration in atomic fraction. The dilation caused by carbon can be estimated from

$$\Delta V = \frac{3}{a \frac{da}{dc}} V$$  \hspace{1cm} (9)
Substitution of the appropriate values into Equation 9 gives \( \frac{\Delta V}{V} = 0.63 \). Thus, on average, the radial strain is 0.21. This quantity can also be estimated from the hard ball model by assuming that the carbon atom has a diameter of about 1.54 Å, its diameter in the diamond lattice and that it can be squeezed into the body-centered position of the fcc unit cell. This gives a misfit of 0.15, which is somewhat less than the lattice parameter estimate. A vacancy on an adjacent lattice site should relax the strain somewhat. However, exactly how much it should relax the carbon dilatation is unknown. For the purposes of this discussion, a value of \( \epsilon = 0.1 \) was assumed for the carbon-vacancy pair. As will be shown later, this gives reasonable agreement with a calculation based on the data. Thus, for the [001] defect

\[
\frac{\Delta V}{V} = -\frac{0.17b}{r} (\sin \theta + \sqrt{2} \cos \theta) \text{ eV (10)}
\]

In order to estimate the size of the interaction constant, it will be assumed that \( \theta = 0 \). On this basis,

\[
u = -\frac{0.17b}{r} \text{ eV (11)}
\]

At \( r = b = 2.49 \times 10^{-8} \text{ cm} \), \( u = 0.17 \text{ eV (3.9 kcal/mole)} \). Thus, the interaction energy is about 0.2 eV (4.6 kcal/mole). The variation of the three energies with angular position are shown in Figure 1.

Next, consider the influence of a dislocation on the carbon-vacancy pair concentration. In Snoek ordering the binding energy \( B \) of Equation 4 should become position dependent. Specifically, \( B = B' + u(r) \) where \( B' \) is the binding energy of a carbon-vacancy pair in a lattice free of dislocation and \( u(r) \), which varies as \( 1/r \), is the position-dependent interaction energy of a carbon-vacancy pair with a dislocation. It should be noted that near the dislocation the binding of vacancies to carbon atoms should vary differently for each of
the three dipole orientations.

The dipole concentration in each of the three orientations can be calculated as follows. Let $c_{cv}$ be the total atom fraction of carbon-vacancy pairs and $(c_{cv})_1$, $(c_{cv})_2$, and $(c_{cv})_3$ the concentrations of pairs in the three possible orientations. After initial ordering, at the beginning of the strain-aging process, we should have

$$c_{cv} = (c_{cv})_1 + (c_{cv})_2 + (c_{cv})_3$$  \hspace{1cm} (12)

where

$$
(c_{cv})_1 = 2c^f_c c^f_v \exp \left( \frac{B' + u}{kT} \right) \hspace{1cm} (13a)
$$

$$
(c_{cv})_2 = 2c^f_c c^f_v \exp \left( \frac{B'}{kT} \right) \hspace{1cm} (13b)
$$

$$
(c_{cv})_3 = 2c^f_c c^f_v \exp \left( \frac{B' - u}{kT} \right) \hspace{1cm} (13c)
$$

and where $c^f_c$ and $c^f_v$ are the initial free carbon and free vacancy concentrations, calculated from Equations 4 and 5. Let us assume that $c^f_c$ and $c^f_v$ are unchanged by the existence of the interaction energies; these may bias $c^f_c$ and $c^f_v$ slightly.

One may also write the concentration of carbon-vacancy pairs as

$$
(c_{cv})_i = c_{cv} \frac{e^{-u_i/kT}}{\sum e^{-u_i/kT}} \quad (i = 1, 2, 3) \hspace{1cm} (14)
$$

or

$$n_i = n_0 \frac{e^{-u_i/kT}}{\sum e^{-u_i/kT}} \hspace{1cm} (15)
$$

where $n_i$ and $u_i$ are the number per unit volume and the interaction energy, respectively, of dipoles in the $i^{th}$ orientation, and $n_0$ is the initial number of dipoles per unit volume.
The principal consequence of the Snoek energy is to increase the concentration of carbon-vacancy pairs in one orientation at the expense of the other two. Figure 2 illustrates the results of a calculation using Equations 12 and 13, and shows that type 1 orientations are favored near the dislocation. At distances greater than 200b, the concentrations of Type 1, 2 and 3 dipoles become nearly equal. The result of the stress-induced ordering of dipoles shown in Figure 2 is to lower the strain energy of the dislocation, thereby causing pinning.

The Shoeck-Seeger model can be utilized to calculate the initial strength of pinning, as measured by \( \Delta \sigma \), due to the ordering of carbon-vacancy pairs. Due to local ordering of the dipoles, the line energy of the dislocation is decreased by an amount \( U_0 \) compared with a dislocation surrounded by randomly oriented dipoles. The decrease in energy \( U_0 \) is the sum of all interaction energies between individual dipoles and the dislocation, and is given by

\[
U_0 = \int_0^{2\pi} \int_0^{R_o} n_t u \, rdrd\theta
\]

where \( R_o \) is approximately one-half the mean dislocation spacing. Substituting Equation 15 into Equation 16 and summing over it gives

\[
U_0 = n_o \int_0^{2\pi} \int_0^{R_o} \frac{ue^{u/kT} - u/kT}{1+e^{u/kT}} \, rdrd\theta
\]

where \( u \) is defined by Equation 6. Since \( u \ll kT \), Equation 17 reduces to

\[
U_0 = \frac{2n_o A^2}{3kT} \int_0^{2\pi} \int_0^{R_o} u^2 \, rdrd\theta
\]

\[
= \frac{2n_o A^2}{3kT} \int_0^{2\pi} \int_0^{R_o} (\sin\theta + \sqrt{2} \cos\theta)^2 \, \frac{dr}{r} \, d\theta
\]

\[
= \frac{2\pi n_o A^2}{kT} \ln \frac{R_o}{r_o}
\]
where \( r_0 \) is approximately the dislocation core radius. This expression is quite similar to Equation 1 derived by Shoeck and Seeger\(^4\) for bcc metals.

Substituting Equation 18 into Equation 2, one obtains

\[
\Delta \sigma = \frac{\mu_n c_{cv} A \sqrt{2}}{b^4} \ln \frac{R_0}{r_0}
\]  

(21)

Thus, \( \Delta \sigma \) due to Snoek ordering of dipoles is essentially temperature independent assuming that the interaction constant, \( A \), does not vary significantly over the temperature range investigated. Additionally, calculations of \( c_{cv} \) indicate that only a 2% decrease of carbon-vacancy pairs occurs over the 100° K interval examined. Using 373° K as a consistent reference temperature, a Schmid orientation factor of 2.5, \( R_0 \) equal to 400\( b \) (one-half mean dislocation spacing),

\[
\Delta \sigma = 1.38 \text{ MPa}
\]  

(22)

This value is in reasonable agreement with the aging curve shown in Figure 3 if one extrapolates to an aging time, \( \sim 1 \text{ second} \), consistent with a vacancy migration distance of approximately 6\( b \), the average carbon atom spacing.

**SUMMARY**

A quantitative model to rationalize the magnitude of the initial stage of the yield point return in nickel-containing carbon has been developed. This calculation takes account of the vacancies generated during plastic deformation, their subsequent trapping by interstitial atoms in a fcc lattice and the pinning of dislocations by these carbon vacancy pairs as they reorient into lower energy orientations in the stress fields of the dislocations.
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REFERENCES


Figure 1. The interaction potential \( u^i \) of a carbon-vacancy dipole with a screw dislocation for \( r = b \) and \( A/b = 0.2 \text{ eV} \).

Figure 2. The computed concentration of carbon-vacancy pairs in each of three possible orientations. \( (B' = 0.3 \text{ eV}, A/b = 0.2 \text{ eV}) \).

Figure 3. The variation of \( \Delta \theta \) with \( \log t \) for specimens aged at 373 K after a 5\% prestrain. The dashed portion of the curve is an extrapolation of \( \Delta \theta \) for aging times approaching one second.
Figure 1.
Figure 3.
THE EFFECT OF DYNAMIC ANNEALING ON DYNAMIC STRAIN AGING PHENOMENA IN COMMERCIAL PURITY TITANIUM

J.R. Donoso*, P.G. Watson** and R.E. Reed-Hill**

ABSTRACT

A study has been made of the effect of dynamic annealing, associated with climb, on the dynamic strain aging phenomena in commercial purity titanium. In specimens deformed at a strain-rate of $10^{-4}$ that have an average grain diameter of about 17 μm, dynamic annealing starts to become important at the temperature of the major work hardening peak maximum. Metallographic evidence supports a conclusion that the shape of the high temperature side of the peak is determined largely by climb controlled processes. Reducing the grain size to 6 μm lowers the temperature, at which dynamic annealing becomes significant, enough so that the work hardening peak, the "blue brittle" ductility minimum and the yield stress plateau are either nearly eliminated or greatly reduced in importance.

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Introduction

Doner and Conrad have pointed out that the stress-strain curves of commercial purity titanium of 22 μm grain size are essentially flat when specimens of this metal are deformed between 850 and 1150 K at strain rates of the order of $10^{-4} \text{s}^{-1}$. This statement is supported by Fig. 1 showing a curve of the average work hardening rate, between strains of 0.5% and 5.0%, plotted against the temperature. Note that slightly above 850 K the work hardening rate approaches zero. Doner and Conrad have suggested that this near zero work hardening rate above 850 K implies a steady state deformation process. They also presented evidence to support a conclusion that the controlling thermally activated mechanism involved climb with Weertman's glide and climb process the most probable process.

We would like to point out that 850 K, above which climb appears to completely control the deformation, is only 75 K above 775 K, the temperature of the major dynamic work hardening peak of commercial purity titanium specimens when deformed at the indicated strain rate with a grain size of about 20 μm. This can be seen with the aid of Fig. 1 where a work hardening versus temperature curve is shown for specimens of a 17 μm grain size. Fig. 1 strongly suggests that the precipitous fall of the work hardening rate, on the high temperature side of this peak, is related to dynamic annealing involving climb. In other words on the high temperature side of the peak dynamic strain aging acting to increase the work hardening rate tends to be nullified by dynamic annealing acting to reduce it.

It can also be postulated that an important factor in this competitive action between dynamic annealing and dynamic strain aging may be the grain size. This is because the stability of the microstructure should be greater with a coarser grain size and thus less subject to dynamic annealing in the temperature range of the work hardening peak. Since the work hardening peak
is only one of a number of identified aspects of dynamic strain aging, there may also be a measurable effect of grain size on other dynamic strain aging phenomena.

On the basis of the above considerations the microstructures of tensile specimens deformed at temperatures in the vicinity of the work hardening peak were investigated by both optical and transmission electron microscopy to determine if evidence of the effects of dynamic annealing on the structure could be observed. The role of grain size in controlling the extent to which dynamic annealing can influence these phenomena was also investigated by pulling specimens of two grain sizes differing significantly in their thermal stability. The results of these investigations are presented in this paper.

**Experimental Procedure**

The composition of the commercial purity titanium hot rolled plate which was used as the starting material is given in Table I. Square bars of approximate dimensions 1.0 cm by 1.0 cm were cut parallel to the rolling direction of the plate and then swaged, without intermediate anneals, to 0.55 cm diameter rods. Threaded end tensile specimens with gage diameters of 0.36 cm and gage lengths of 1.65 cm were machined from the rods, and annealed under a dynamic vacuum of about $1.3 \times 10^{-3}$ Pa to the desired grain sizes as defined by the mean grain intercept. As will be explained later, most specimens for the tensile tests were annealed to two grain sizes, 6 μm and 17 μm. A few specimens were annealed to a 43 μm grain size.

Thin foils, suitable for transmission electron microscopy, were prepared from specimens prestrained selected amounts at several temperatures. Metallographic specimens were prepared following standard procedures.

**Tensile Testing:** Tensile tests were conducted between 300 and 900 K using an
Instron TT-C tensile machine. All tests were made in an ultra-high purity, oxygen gettered argon atmosphere. The nominal strain-rate was $5.1 \times 10^{-4}\text{ s}^{-1}$. For purposes of measuring the strain-rate sensitivity, a strain-rate differential was used involving a factor of 10. The strain-rate sensitivity was defined by the relation $n = \frac{d \ln \sigma}{d \ln \dot{\varepsilon}}$ where $\sigma$ was the flow stress and $\dot{\varepsilon}$ the strain-rate.

Flow stress transients appeared when the strain-rate was changed in the approximate temperature interval from 600 to 800 K. Fig. 2 illustrates schematically a situation where a transient developed due to a strain rate change, and shows the two possible stresses related to the higher strain-rate, namely $\sigma^1$, the extrapolated stress, and $\sigma^\prime\prime$, the instantaneous or transient stress. The extrapolated flow stress was used to determine the strain-rate sensitivity.

**Experimental Results**

**Annealing:** The variation of the grain size with annealing temperature of the annealed swaged titanium rod is shown in Fig. 3. The solid curve corresponds to specimens given 1/2 hour anneals. This curve shows that to obtain a 17 $\mu$m grain size, like that of the specimens whose work hardening data are given in Fig. 1, an annealing temperature of 1073 K is required. This is close to the transformation temperature at 1155 K. On the other hand, at 773 K, near the temperature of the work hardening peak in Fig. 1, a half hour anneal results in a grain size of 4.5 $\mu$m, while a one hour anneal increased the grain size to 6 $\mu$m. One hour is about equivalent to the exposure at the testing temperature that a specimen is subjected to when it is tested. Thus a specimen annealed for 1 hour at 773 K to a grain size of 6 $\mu$m should have a structure much less stable for testing in the vicinity of the work hardening peak, 600 to 900 K, than one annealed at 1073 K to a 17 $\mu$m grain size. Consequently, it was decided to limit the grain sizes investigated to 6 $\mu$m and 17 $\mu$m. However, a few tests were made with specimens annealed to a 43 $\mu$m grain size which required 26 hours...
at 1123 K to achieve.

**Dynamic Strain Aging Phenomena**: Six prominent aspects of dynamic strain aging have been identified. These are:

1. The work hardening peak,
2. The yield stress plateau,
3. The Portevin-Le Chatelier effect,
4. The strain-rate sensitivity minimum,
5. The "blue-brittle" effect,

The effect of reducing the grain size, and thus the resistance of the structure to dynamic annealing, on these six aspects of dynamic strain aging will now be considered.

1. **The work hardening peak**: The curve of the work hardening as a function of temperature for 6 μm grain size specimens is plotted below the 17 μm curve in Fig. 1. It is clear from this curve that the 773 K work hardening peak is effectively eliminated if the grain size is decreased to 6 μm. Fig. 1 also shows several data points obtained with 43 μm grain size specimens. The primary feature that these latter reveal is approximately a 30 K displacement of the high temperature side of the work hardening peak to higher temperatures. This is consistent with a greater stability of the 43 μm structure.

2. **The yield stress plateau**: Curves showing the variation of the lower yield stress with temperature for tensile specimens of both the 6 μm and 17 μm grain sizes are shown in Fig. 4. The smaller grain size specimens exhibited a generally higher yield stress except for temperatures in excess of 700 K where the two yield stresses become nearly equal. The data from the 17 μm specimens
show a well defined yield stress plateau covering the temperature range from about 600 to 750 K. The 6 μm grain size curves exhibits only an inflection corresponding to a plateau. In this material the plateau is nearly missing.

3. The "blue brittle" effect: Tensile elongation versus temperature data for both the 6 μm and 17 μm grain size specimens are given in Fig. 5. This diagram shows that reducing the grain size from 17 μm to 6 μm effectively eliminates the "blue brittle" ductility minimum.

4. The Portevin-Le Chatelier effect: Discontinuous or serrated plastic flow, the Portevin-Le Chatelier effect, is exhibited by the coarser grained material from approximately 675 to 730 K. The finer grained 6 μm material also showed serrations on its stress-strain curves. They were, however, less pronounced.

5 and 6. The strain-rate sensitivity minimum and flow stress transients: Differential strain-rate tests were carried out at some temperatures on the 6 μm grain sized specimens and the strain-rate sensitivity values thus obtained are plotted in Fig. 6. In this diagram they are compared with earlier data due to Garde for 17 μm grain size titanium specimens. Fig. 6 shows that the 6 μm specimens still exhibit a well defined strain-rate sensitivity minimum. The strain-rate sensitivity, however, does not go effectively to zero as it does with the 17 μm specimens. This effect is further illustrated in Fig. 7 where the results of an order of magnitude change in strain-rate on a 6 μm and a 17 μm grain sized specimen at 760 K are illustrated. Note that at both grain sizes an increase in strain-rate first produced a small transient peak in the flow stress curve while a decrease in strain-rate produced a small minimum. Generally speaking it was observed that decreasing the grain size did not eliminate the tendency to produce flow stress transients on a
change in strain-rate but merely tended to reduce their size. Also to be noted is that in the 17 μm specimen a change in strain-rate did not result in a significant change in the level of the flow stress, in conformity with a near zero strain-rate sensitivity, while at 6 μm a change in strain-rate did result in a finite change in the flow stress.

Metallography: The variation of the microstructure with deformation temperature in the 17 μm specimens is shown in Fig. 8. The three optical micrographs of this figure show structures in fractured specimens at points close to the fracture while the TEM picture represents a specimen strained 5%. Fig. 8a shows the structure developed at 760 K, a temperature slightly below that of the work hardening peak maximum. In this specimen the grains are elongated in the direction of the tensile strain and the grain boundaries remain smoothly curved. The optical microscope accordingly indicates a structure which has not undergone visible high temperature dynamic annealing. However, at 790 K, only 15° above the peak temperature, one begins to see evidence of grain boundary mobility. This is shown in Fig. 8b where small serrations have begun to appear along the grain boundaries. At 860 K in Fig. 8c the effects of dynamic annealing are more readily apparent. The grain boundaries are now strongly dentated and in this photograph made with polarized light a number of sub-grain boundaries are clearly indicated. Finally Fig. 8d shows a TEM micrograph in which a well defined sub-grain boundary may be observed in a foil taken from a 17 μm grain sized specimen deformed at 860 K to 5% strain.

Fig. 9 shows a set of photomicrographs from specimens with a 6 μm grain size. The (a) member of this set shows the annealed undeformed structure. Fig. 9b shows the structure after deformation at 610 K, a temperature just below that where the average work hardening rate curve for the 6 μm specimens in Fig. 1 begins to deviate widely from the 17 μm curve. The deformed structure
shows little or no evidence of high temperature dynamic annealing at this temperature as might be expected. On the other hand, at 750 K, as shown in Fig. 9c, there is strong evidence for annealing during deformation. This is supported by the TEM micrograph in Fig. 9d made from a foil taken from the uniformly strained portion of the gage section of the fractured 750 K specimen. Here a well defined substructure is indicated.

Discussion

Metallurgical Evidence of High Temperature Dynamic Annealing: The metallurgical evidence from the 17 μm grain size specimens in Fig. 8 supports the hypothesis that high temperature dynamic annealing occurs on the high temperature side of the work hardening peak. Just below the work hardening peak temperature, the deformed microstructure as shown in Fig. 8a, has the characteristic appearance of low temperature deformation. However, at 790 K, only 15 K above the work hardening maximum, the boundaries tend to become dentated and the polarized light microscope begins to show evidence of subgrain boundaries (Fig. 8b). Dentated grain boundaries and subgrains are strong evidence for dynamic annealing. At 85° above the peak (Fig. 8c) where the work hardening has decreased to about half that at the peak, the boundaries become strongly dentated and the polarized microscope shows stronger evidence of a subgrain structure. This substructure is also evident under the TEM (Fig. 8d).

Normally one expects that the temperature dependence of the work hardening peak should exhibit an activation energy equal to that for diffusion of the solute responsible for the dynamic strain aging. In the present case this might be expected to be oxygen. However, since the high temperature side of this work hardening peak appears to be closely associated with climb it is possible that the peak temperature is actually determined by the onset of this climb.
The activation energy for the work hardening peak present in commercial purity titanium has been given as 57 Kcal/mole by Conrad, Doner and De Meester based on the data of Santhanam. Doner and Conrad have also concluded that the activation energy for self-diffusion or climb in titanium is 57 Kcal/mole. These data support the hypothesis that the work hardening peak temperature is controlled by climb. The conclusion cannot be definite because the activation energy for the diffusion of oxygen in titanium is not well defined and some authors have placed it close to 57 Kcal/mole. However, based on an analysis of the available data in the literature Doner and Conrad concluded that the activation energy for the diffusion of oxygen in titanium probably lies between 45 and 52.5 Kcal/mole. It is interesting that Santhanam's measurement for the activation energy for the first appearance of serrations in his titanium specimens gave 41 Kcal per mole. The activation energy for the initial appearance of serrations has been found in a number of cases to correlate well with the activation energy for the diffusion of the species responsible for strain aging. Although Santhanam's 41 Kcal per mole activation energy for the onset of serration is lower than the 45 to 52.5 Kcal per mole value for the diffusion of oxygen in titanium one has to take into consideration two factors. First the diffusion coefficient for oxygen is not known with certainty and second 41 Kcal differs significantly from the 57 Kcal per mole value corresponding to the work hardening peak. This difference strongly suggests that the onset of serrations and the work hardening peak involve two different processes and from this point of view the assumption that the work hardening peak temperature dependence conforms to climb is supported.

The data in Fig. 9 shows that at 610 K the microstructure of the 6 μm grain size specimens is characteristic of low temperature deformation; i.e., deformation not accompanied by significant dynamic annealing. However, at 25° below the work hardening peak maximum, 750 K, where, in the 17 μm specimens,
dynamic annealing was not observed, the 6 μm specimen shows clear evidence of
dynamic annealing. This correlates well with the fact that, as may be seen in
Fig. 1, the work hardening rate at this temperature is only about 50% of its
value at 610 K and more significantly is only about 40% of that in the 17 μm
grain sized specimen at this same temperature. One may conclude that dynamic
annealing at 750 K produces a significant effect on the work hardening rate
in 6 μm specimens.

Not all aspects of dynamic strain aging are equally affected by reducing
the grain size until dynamic annealing is encouraged. The most significant
changes in the dynamic strain aging phenomena when one goes from the 17 μm
to the 6 μm grain size specimens, occur in the amplitudes of the work hardening
peak and the "blue brittle" ductility minimum. Lowering the grain size also
greatly reduces the size of the yield stress plateau as may be seen in Fig. 4.

It would appear from the above that the strongest effects of dynamic
annealing occur with respect to those aspects of dynamic strain aging primarily
associated with work hardening. These are the work hardening peak, the yield
stress plateau and the "blue brittle" ductility minimum. In this regard it
should be noted that the yield stress is a flow stress and therefore associated
with a small but significant amount of work hardening. At the same time the
"blue brittle" ductility minimum in titanium can be rationalized in terms of
the displacement of the work hardening peak to higher temperatures when the
strain-rate is increased. As a result of this, at the "blue brittle" temper-
ature when a neck forms, with a concomitant increase in strain-rate in the
shorter effective gage length at the neck, there is a resulting decrease in
the work hardening rate at the neck. This acts to sharpen the neck so that
its length is shortened. The result is a decrease in total elongation.

The fact that dynamic annealing has an apparently stronger effect on
aspects of dynamic strain aging related to work hardening than on the other
dynamic strain aging aspects, in the 6 \textmu{}m specimens, can be rationalized. This is because the observed work hardening rate is a net rate. In other words dynamic strain aging normally acts to increase the rate of accumulation of dislocations during deformation while dynamic annealing tends not only to alter the distribution of dislocations but also to eliminate dislocations. Thus dynamic strain aging adds a positive component to the work hardening rate whereas dynamic annealing adds a negative component. Thus above roughly 600 K the strong component of dynamic annealing in the 6 \textmu{}m specimens effectively eliminates those aspects of dynamic strain aging associated with work hardening.

\textbf{Summary and Conclusions}

1. The fact that climb has been proposed to control deformation in alpha titanium above 850 K implies that the precipitous fall of the work hardening rate on the high temperature side of the dynamic strain aging work hardening peak is due to climb with climb tending to nullify the effects of dynamic strain aging.

2. The conclusion that climb influences the shape of the high temperature side of the work hardening peak is supported by metallography. With increasing temperature above the work hardening peak maximum the structure shows increasing evidence of dynamic annealing with grain boundaries becoming more serrated or dentated and evidence for subgrain formation increasing.

3. The activation energy corresponding to the strain-rate dependence of the work hardening peak temperature is 57 Kcal/mole which is in good agreement with estimated values of the activation energy for self diffusion. This suggests that the peak temperature is actually determined by the onset of climb. In other words it is not representative of the strain aging phenomena.

4. With decreasing grain size there is a significant decrease in the stability of the commercial purity titanium microstructure with respect to dynamic
annealing. Reducing the grain size from 17 μm to 6 μm lowers the temperature, at which dynamic annealing phenomena becomes important, enough to eliminate the work hardening peak. It also greatly reduces the significance of other aspects of dynamic strain aging. The effect is strongest on those aspects related to work hardening. Thus the "blue brittle" ductility minimum is effectively removed and the yield stress plateau is nearly eliminated.

Acknowledgement

The authors greatly appreciate the financial support of the Energy Research and Development Administration under contract No. AT-(40-1)-3262.
Figure Captions

Figure 1. The average work hardening rate versus the temperature. The upper curve corresponds to data obtained from specimens with a 17 μm grain size. The lower curve to specimens with a 6 μm grain size. The work hardening rate is defined in terms of the increase in flow stress from 0.5 to 5.0% strain.

Figure 2. Schematic of a change in strain-rate test. The two stresses that can be used at the higher strain-rate are designated \( \sigma_2' \) (extrapolated) and \( \sigma_2'' \) (instantaneous).

Figure 3. The variation of the grain size of commercial purity titanium with the annealing temperature and time.

Figure 4. The variation of the lower yield stress with temperature for tensile specimens of both the 6 μm and 17 μm grain size.

Figure 5. These curves of the total elongation in a tensile test versus the temperature show that the "blue brittle" ductility minimum, evident in the 17 μm data, is effectively absent in the 6 μm data.

Figure 6. Plots of the strain rate sensitivity parameter "n" versus the temperature. The 6 μm grain size specimens still exhibit a well defined strain-rate sensitivity minimum.

Figure 7. Illustrating the effect of an order of magnitude strain-rate change on the stress-strain curves of a 6 μm and a 17 μm grain sized titanium specimen, at 760 K where the strain rate sensitivity is a minimum.

Figure 8. The variation of the microstructure with deformation temperature in specimens with a 17 μm grain size. (a) 760 K, just below the work hardening peak the structure is thermally stable. (b) at 790 K, the grain boundaries are slightly dented. (c) at 860 K, 85° above the work hardening peak, the boundaries are strongly serrated and a sub-grain structure is revealed by the polarized light microscope. (d) a well defined sub-grain boundary as seen in the 860 K specimen under the transmission electron microscope.

Figure 9. The variation of the microstructure with deformation temperature in 6 μm grain size specimens. (a) the annealed starting structure. (b) a specimen deformed at 610 K where the structure is stable. (c) at 750 K, the temperature of the work hardening peak for 17 μm grain size specimens, the deformed structure is unstable. (d) the sub-grain structure as revealed by the TEM in a specimen deformed at 750 K.
TABLE I

Chemical Composition for Commercial Purity Titanium

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</table>
Figure 1

\[ \frac{\Delta \sigma}{\Delta \varepsilon}, \times 10^3 \text{ MPa} \]

- 6\( \mu \)
- 17\( \mu \)
- 43\( \mu \)

Temperature, K
Figure 2
Figure 3
\[ \varepsilon = 5.1 \times 10^{-4} \text{ sec}^{-1} \]

Figure 4

- L.Y.S., 6 \( \mu \text{M} \)
- L.Y.S., 17 \( \mu \text{M} \)

Stress, MPa vs Temperature, K
Figure 7

\[ \dot{\varepsilon}_2 = 10 \dot{\varepsilon}_1 \]

760 K, 6\(\mu\)M

760 K, 17\(\mu\)M
Figure 8
Figure 8
Figure 9

(a) 524X

(b) 400X
SLOW STRAIN-RATE EMBRITTLEMENT AND ITS RELATION
TO STRAIN-AGING IN REFRACTORY METALS

Scientific Report

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INTRODUCTION

Interstitial solutes such as hydrogen, oxygen, nitrogen and carbon can strongly influence the mechanical properties of certain metals. Prominent among the phenomena that interstitials can invoke are dynamic strain-aging and slow strain-rate embrittlement. In both cases, it is recognized that diffusion of interstitials plays an important role. Thus, it is generally agreed that in dynamic strain-aging the interstitial atoms diffuse to and react with mobile dislocations. A number of effects upon the stress-strain behavior are produced by this interaction including: 1) serrated plastic flow commonly known as the Portevin-LeChatelier effect, 2) the "Blue brittle effect," 3) plateaus or even peaks in plots of the yield stress versus temperature, 4) abnormal and rate dependent work hardening (this is frequently revealed in terms of a peak in some aspect of the work hardening when plotted as a function of the temperature. For example, a peak in a plot of ultimate tensile stress versus temperature often results from dynamic strain-aging), 5) abnormally low strain-rate sensitivity, and 6) transients on the stress-strain curve when the strain-rate is altered. In the case of slow strain-rate embrittlement, on the other hand, it is often assumed, following Troiano, that the effect is due to the diffusion of the interstitial towards the region of triaxial stress concentration in advance of a
crack front. The resulting increase in concentration of the interstitial ahead of the crack is then believed to cause local embrittlement and to facilitate the advancement of the crack.

Because in a given metal both classes of phenomena can be invoked by the same kind of interstitial and both show a dependence upon the ability of the interstitial to diffuse, it is reasonable to assume that there may be further interrelations. Supporting this concept is the fact that the "blue brittle" effect is a recognized aspect of dynamic strain-aging. It is interesting to note that this is an embrittlement phenomenon that apparently does not involve the Troiano hypothesis. Further, from a more general point of view, fracture has to be considered as the ultimate result of the plastic flow processes preceding it; the abnormal nature of the deformation that occurs during dynamic strain-aging could well modify the fracture processes.

As will be demonstrated, admittedly on the basis of limited data, there appears to be a good empirical correspondence, in specimens deformed at conventional strain-rates, between the temperature intervals in which one observes dynamic strain-aging on the one hand and slow strain-rate embrittlement on the other. The existence of such a correlation implies that it might be profitable to look for direct relations between the strain-aging and the embrittlement phenomena.
In the first paragraph above, six aspects of dynamic strain-aging were listed. Of these the third and fourth, as exemplified by the yield stress plateaus and work hardening peaks, normally cover the temperature range inside which all the other aspects of dynamic strain-aging are observed. Furthermore, they are also aspects of dynamic strain-aging that tend to be more generally reported in the literature. For the purposes of this survey, the temperature intervals over which the yield stress plateaus or work hardening peaks extend will be considered a measure of the temperature interval in which dynamic strain-aging phenomena are significant.

With regard to defining the temperature interval inside which slow strain-rate embrittlement occurs, curves of either the reduction in area versus the temperature or curves of the elongation versus the temperature will be employed. In this case, the range of embrittlement can be described in terms of the temperature range within which the ductility exhibits a measurable loss in magnitude.

While it would appear that there should be a great deal of information available in the literature that could be used for the present purposes this is not so. Few investigators have included data in their papers covering both strain-aging and embrittlement phenomena. There are several factors involved in this problem. First, slow strain-rate embrittlement has until
recently been considered primarily a phenomenon associated with hydrogen in body-centered cubic transition metals. Because of the very small values of the activation energies associated with the diffusion of hydrogen in these metals, the hydrogen embrittlement phenomena tend to occur at temperatures well below room temperature. This is a region where the stress rises to high levels and the ductility is normally very small in body-centered cubic metals as shown very graphically in Fig. 1 from a paper by Eustice and Carlson for the case of vanadium containing hydrogen. Note that in part "b" of this figure, corresponding to specimens containing 50 ppm of hydrogen, fracture occurs below -50°C as soon as the lower yield stress is reached. Obviously, in these specimens most of the aspects of strain-aging such as the work hardening peak, serrated yielding, the "blue brittle" effect and the strain-rate sensitivity minimum cannot be observed because the stress-strain curve ends at the yield point. All that can be determined is a yield stress plateau. Thus, in metals embrittled by hydrogen, the lack of data corresponding to strain-aging has been, in large measure, due to the fact it has not been possible to observe the strain-aging phenomena in specimens containing hydrogen levels corresponding to severe embrittlement. On the other hand where the interstitial has been oxygen, nitrogen or carbon, i.e.,
not hydrogen, the major concern has been to investigate strain-aging phenomena. Here little concern has been given to embrittlement. A factor in this regard may be that strain-aging phenomena can be induced at concentrations of the interstitial too low to show a significant effect of the interstitial on the ductility parameters. These low concentration levels normally correspond to those found in commercially pure metals. Thus, strain-aging phenomena have been generally studied in niobium containing less than 0.1 at% oxygen. It has been shown, however, that at conventional strain-rates ($10^{-3}$ to $10^{-4}$ s$^{-1}$), slow strain-rate embrittlement only becomes significant at oxygen concentrations in excess of 0.5 at%. Thus, slow strain-rate embrittlement is not a significant factor during tensile deformation at conventional strain-rates in niobium containing commercial purity levels of oxygen. This is not to imply that slow strain-rate embrittlement is not a significant phenomenon in these materials. Niobium can react rapidly with oxygen even in a moderately good vacuum ($10^{-4}$ Torr) at temperatures in excess of 400°C. The surface of a niobium specimen can accordingly attain a composition in excess of 0.5% oxygen with a concomitant tendency to undergo surface cracking during tensile loading. An example is shown in Fig. 2. With prolonged exposure to stress in this temperature range progressive embrittlement is to be expected as the surface cracks progressively reduce the cross-section area allowing oxygen to
penetrate further and further into the specimen.

The Nickel-Hydrogen System

There is one notable exception where hydrogen embrittlement and dynamic strain-aging data have been reported in detail involving the same set of specimens. This is in a paper by Windle and Smith** who investigated polycrystalline nickel specimens of 140 μm grain size charged with 9 ppm of hydrogen (0.05 at %). Hydrogen at this level produces a significant Portevin-LeChatelier effect and it also has a strong influence on the work hardening rate. Because hydrogen does not increase the initial yield stress, the effect of hydrogen on work hardening is easy to evaluate. This is because, at the yield stress, the flow stress at a given temperature and strain-rate is the same in a charged specimen as in an uncharged specimen. Thus, the difference in flow stress between a charged and uncharged specimen, at a given strain, is a measure of the additional work hardening caused by the hydrogen. Fig. 3 shows the variation with temperature of this flow stress difference, $\Delta \sigma$, measured at 0.20 strain for data obtained at two different strain rates differing by a factor of 25. This diagram shows a well defined work hardening peak typical of dynamic strain-aging. This peak is strain-rate dependent in that it shifts to a lower temperature at the slower strain-rate. The arrows
designated LCT and HCT on each of the two curves correspond to the lower and upper critical temperatures that limit the region within which serrated flow or the Portevin-LeChatelier effect occurs. Note that the temperature interval in which the Portevin-LeChatelier effect is observed is only about one-third as wide as the range of temperatures in which abnormal work hardening is observed. The authors have made an interesting observation relative to the dip in the work hardening rate that occurs just to the right or on the high temperature side of the LCT. They argue that at this point deformation first becomes inhomogeneous since at this temperature the nucleation and growth of Luders bands first begins to occur. The deformation rate in a Luders band can be many times higher than the average or applied strain-rate. This results in an effective increase in strain-rate that should be accompanied by a decrease in the work hardening rate. On this basis it could be argued that the point corresponding to the minimum work hardening rate defines a temperature above which deformation occurs only in the Luders bands and below which some general deformation occurs in addition to that in the bands.

An important aspect of Fig. 3 worth noting is the wide temperature interval within which hydrogen has a strong influence on the work hardening rate. That 9 ppm (0.05 at %) of hydrogen
has an equivalent effect on the ductility parameters is demonstrated in Figs. 4 and 5. The first of these figures shows how the elongation varies with temperature. Before continuing it should be noted that the curves in Figs. 3, 4 and 5 correspond to data obtained from the same specimens.

The size of the ductility minimum in Fig. 4 increases with decreasing strain-rate as is typical of slow strain-rate embrittlement. This increase in embrittlement with decreasing deformation rate is even more evident in Fig. 5 which shows the reduction of area as a function of temperature for five strain-rates. In terms of this parameter, it is evident that the rate dependence of the ductility is strongest on the high temperature side of the ductility minimum.

It may be concluded from Figs. 3, 4 and 5 that in the case of nickel specimens charged with 9 ppm of hydrogen there is a good correlation between the temperature interval associated with the work hardening peak and that associated with the ductility minimum. Something should be said, however, about the nature of the embrittlement which is intergranular. Hydrogen charged single crystals were not embrittled and failed by pulling down to a chisel edge fracture. Cracks in polycrystalline nickel charged with hydrogen tend to nucleate at three-grain edges. This is analogous to the intergranular fracture nucleation normally associated
with high temperature creep. Evidence for grain boundary sliding was also observed by Windle and Smith,\(^3\) which further implies that hydrogen may be inducing fractures similar in character to high temperature intergranular creep fractures.

Of more immediate interest is the fact that near 0°K and above, evidence was found which suggested that cracks appeared to be propagating by the nucleation of smaller cracks in front of the crack front. An example is shown in the photomicrograph in Fig. 6. This implies that the intergranular crack propagation in this high temperature interval may follow a mechanism of the type proposed by Troiano.\(^2\) That is one where the hydrogen diffuses to the region of stress concentration in advance of the crack front.

**The Niobium-Oxygen System**

The fact that oxygen is capable of causing slow strain-rate embrittlement in niobium\(^6\) is illustrated in Figs. 7 and 8. In Fig. 7 the effect of oxygen concentration on the ductility is shown by plotting curves of the reduction in area as function of temperature for four levels of oxygen concentration. For specimens deformed at a strain-rate of \(5 \times 10^{-4}\) s\(^{-1}\) and concentration levels in excess of about 0.5 at \% oxygen, a ductility minimum appears. The effect of strain-rate on the
ductility minimum is shown in Fig. 8. Note that the embrittlement increases with decreasing strain-rate as expected for slow strain-rate embrittlement. For comparison purpose the analogous curves of Hardie and McIntyre, for niobium embrittled by hydrogen, are shown in Fig. 9. These reduction in area versus temperature curves include data from specimens tested at several strain-rates and two levels of hydrogen concentration. The analogy between the data in Figs. 7 and 8 with that in Fig. 9 is excellent. There is one basic difference, however, the hydrogen embrittlement minimum occurs below room temperature while the oxygen embrittlement interval occurs well above room temperature. This is consistent with a lower activation energy for the diffusion of hydrogen in niobium than that for the diffusion of oxygen in niobium.

As may be seen in Fig. 7 the ductility minimum has an upper temperature limit at about 950°K and a lower temperature limit at approximately 450°K. The flow stress at 5% strain, as a function of the temperature for specimens doped with the highest level of oxygen, 2.31 at % is shown in Fig. 10. The curve exhibits a work hardening peak that covers almost the same temperature interval as that corresponding to the ductility minimum for these same specimens shown in Fig. 7. This work hardening peak can be seen more clearly in Fig. 11 where the
logarithm of the flow stress is plotted as a function of the temperature. Normally a semi-log plot of the flow stress versus the temperature tends to yield a straight line. On the other hand, a dynamic strain-aging work hardening peak usually produces a deviation of the flow stress-curve from linear behavior. Thus, Fig. 11 implies a work hardening peak that starts at about 400°K and extends to about 950°K.

**The Role of the Softening Temperature**

Aspects of dynamic strain-aging, such as abnormal work hardening and abnormal yield stresses depend on the maintenance of a stable dislocation structure. Since high temperature recovery tends to dissipate such structures both the work hardening peak and the yield stress plateau should tend to disappear once the rate of recovery becomes truly significant.

As a test of the above hypothesis consider the vanadium-nitrogen system. Fig. 12 shows the ultimate tensile stress versus temperature curves of Thompson and Carlson corresponding to six concentration levels of nitrogen. All of the curves exhibit a work hardening peak extending from roughly 500°K to 850°K. This temperature range of 350° is smaller than the approximately 600° interval shown for the work hardening peak in the niobium-oxygen system in Figs. 10 and 11. The upper temperature limit of 850°K for the vanadium-nitrogen system, however, corresponds to about
0.4 $T_m$ where $T_m$ is the melting point of vanadium. At this homologous temperature it is reasonable to expect that high temperature recovery phenomena (climb processes) could play a strong enough part during plastic deformation to cause recrystallization.

The Titanium-Oxygen System

The titanium-oxygen system offers an even better example of a system in which softening limits the high temperature side of both the work hardening peak and the slow strain-rate embrittlement ductility minimum. The work hardening peak in commercial purity titanium is shown in Fig. 13. In this case, the difference in flow stress, $\Delta \sigma = \sigma_{5.0} - \sigma_{0.5}$, between the stress at 5% and at 0.5% plastic strain is plotted as a function of the absolute temperature. The principal interstitial impurity in the C.P. titanium metal was oxygen as may be seen in Table I. The work hardening versus temperature curve of high purity (Marz Grade MRC) titanium is also shown in Fig. 13. This demonstrates that the peak is due to the impurities since the peak is suppressed in the higher purity curve. The microstructure of a C.P. titanium specimen deformed at 860°K is shown in Fig. 14. This corresponds to a temperature on the high temperature side of the work hardening peak in Fig. 13. All of the grain boundaries in this
microstructure are dentated implying that the boundaries were migrating during deformation and that the microstructure was unstable. We may conclude that this specimen was deforming at a temperature where softening during deformation was a significant factor.

Curves of reduction in area as a function of temperature are plotted in Fig. 15 for C.P. titanium specimen is deformed at 5 different strain-rates between $10^{-1}$ and $10^{-6}s^{-1}$. These curves show a ductility minimum that increases in magnitude with decreasing strain-rate. Note that at the fastest strain-rate there is no minimum. The significant feature of these curves is the fact that the minimum is narrow compared to that observed in the niobium-oxygen and niobium-hydrogen systems as shown in Figs. 7 and 9 respectively. The sharp rise of ductility on the high temperature side of the minimum conforms to the effect of softening on increasing the ductility. Fig. 14 supports this conclusion since at a strain-rate of $2.7 \times 10^{-4}s^{-1}$ the temperature of 860 K corresponding to a structure strongly influenced by recovery also corresponds to a return to maximum ductility. On the other hand Fig. 17, which shows a microstructure at the ductility minimum, indicates a stable microstructure. Thus, the return of ductility is accompanied by a pronounced increase in dynamic recovery.
As pointed out in another publication the embrittlement phenomenon in titanium due to oxygen has a close association with dynamic strain-aging. Thus, the reduction in area minimum occurs only about 25°K above the "blue brittle" elongation minimum. Furthermore, an interesting relationship exists between the reduction-in-area minimum and the way that the work hardening rate depends on the strain-rate. This can be seen with the aid of Fig. 17 showing the variation of the average work hardening rate $\Delta \sigma/\Delta \varepsilon$, plotted as a function of the strain-rate for a set of specimens deformed at 760°K. As may be seen in Fig. 15, the ductility minimum occurs at 760°K when the strain-rate is $2.7 \times 10^{-4}$. This strain-rate is almost exactly that of the peak in the work hardening rate versus strain-rate curve in Fig. 17. This implies that the increase in strain-rate that occurs in the neck once it forms is accompanied by a drop in the rate of work hardening. This should cause the neck to become strongly localized. In the titanium specimens fracture occurred by microvoid coalescence. The development of pores in the necked region should also tend to increase locally the strain-rate thereby further decreasing the work hardening rate and promoting a fracture with a restricted ductility. The net result could well be a loss in reduction-in-area as catastrophic fracture occurred in this restricted region of high strain-rate and low work hardening rate.
Molybdenum-Carbon

In the Moly-Carbon system, carbon is thought to be responsible for the DSA and SSRE phenomena that occur near 1800°K. In a manner similar to the Nb-0 system, both groups of phenomena appear at elevated temperatures consistent with the high activation energy for diffusion of carbon in Molybdenum. In the Mo-C system, however, the embrittled region covers only a narrow temperature span due to recovery phenomena that begin at a temperature well down into the DSA or SSRE range. 9

Wilcox, Gilbert and Allen 9 investigated the tensile properties of Mo-TZM (composition in Table II) over the temperature range of 500° to 2000°K at three strain rates and three levels of carbon. The results of these tests are shown in Fig. 18. The increase in work hardening in the region of 1200°K to 1800°K is evident from the yield stress and ultimate tensile strength curves. Also apparent is the influence of the strain-rate on the work hardening peak typical of a DSA temperature regime. The embrittled region (region of reduced reduction in area) occurs generally coincident with the work hardening peak and increases in severity of embrittlement as the strain-rate is decreased. Other attributes of DSA also present in this temperature range are serrated yielding and blue brittle necking.
Thus, this investigation has found most of the DSA associated phenomena, including SSRE, localized in a single temperature range.

In a manner similar to the Ni-H system, within this embrittled temperature range the mode of fracture becomes strongly intergranular as cracking extends the full length of the gage section. Outside of the embrittled range the fracture is ductile with corresponding reductions in area near 100%.

The properties of the carbide strengthened Moly alloys in this temperature range have been ascribed to DSA or alternately to strain induced precipitation on dislocations which is a form of DSA. However, disagreement exists as to the exact nature of the carbide or carbides responsible for the DSA phenomena.

The mechanism proposed by Wilcox et al to account for the deformation and fracture characteristics in this regime is shown schematically in Fig. 19. They propose that precipitation of carbide occurs during deformation, an observation supported by Raffo resulting in preferential strengthening of the grain matrix over the grain boundaries. This shifts the deformation and fracture processes to the grain boundaries with the resultant change in fracture mode. It is interesting to note that, in this and the Ni-H system as opposed to the Nb-0 or Nb-H system, similar initial conditions (i.e., abnormally high
work hardening) result in radically different modes of embrittlement and subsequent fracture indicating that there is at least one additional factor, aside from the high work hardening rate, which determines the fracture mode.

Thus, it would appear in this system, that intergranular fracture and the associated ductility minimum are possibly related to dynamic strain-aging.

Summary

The available data for comparing slow strain-rate embrittlement with dynamic strain-aging phenomena are very limited. Systems in which both classes of phenomena have been studied in any detail include only nickel-hydrogen, niobium-oxygen, molybdenum-carbon, and titanium-oxygen (C.F. titanium). In all four of these systems, however, there is a good correspondence between the temperature intervals in which dynamic strain-aging and slow strain-rate embrittlement appear in specimens deformed at conventional strain-rates ($10^{-3}$ to $10^{-4}$s$^{-1}$). An important factor in determining the extent of the temperature range in which slow strain-rate embrittlement and dynamic strain-aging are observed is the softening temperature, above which high temperature dynamic recovery becomes significant. The softening temperature can form the upper temperature limit for both classes of phenomena. In the Nb-0 system the softening temperature lies above
the embrittlement dynamic strain-aging range. This is not true in the Ti-O system where both the ductility minimum and work hardening peak are narrow.

The correlation between the ranges of temperature in which dynamic strain-aging and slow strain-rate embrittlement phenomena are observed implies that there may be other connections between the two types of effects.
REFERENCES


**TABLE 1**

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Fig. 1 - Load-elongation curves of vanadium at different temperatures with and without hydrogen present. From Eustice and Carlson.

Fig. 2 - Surface cracking observed in a high purity niobium specimen deformed 5% in an ungettered impure argon atmosphere at 820 K. Strain-rate $5 \times 10^{-4}s^{-1}$. Magnification 1600 times. From Donoso and Reed-Hill.
Fig. 3 - The increase in flow stress, in nickel, at 20% nominal strain due to hydrogen, as a function of testing temperature. From Windle and Smith.  

Fig. 4 - The temperature dependence of the maximum uniform elongation of hydrogen-containing nickel specimens for two strain-rates. From Windle and Smith.
Fig. 5 - The influence of temperature and strain-rate on the reduction in area at fracture for hydrogen-containing nickel specimens. From Windle and Smith.

Fig. 6 - Section through a specimen showing crack nucleation ahead of an intergranular crack in hydrogen bearing nickel. From Windle and Smith.
Fig. 7 - The effect of oxygen concentration on the reduction in area versus testing temperature curves of niobium. Strain-rate $5 \times 10^{-4} \text{s}^{-1}$. From Donoso and Reed-Hill.

Fig. 8 - The reduction in area versus testing temperature for niobium specimens, containing 0.85% oxygen, deformed at two strain-rates. From Donoso and Reed-Hill.
Fig. 9 - The effect of 25 wt ppm hydrogen on the reduction in area of niobium as a function of testing temperature at various strain-rates.
Fig. 10 - Flow stress, at 5% strain, versus testing temperature for niobium containing 2.31 at% oxygen.
Fig. 11 - Semi-logarithmic plot of flow stress, at 5% strain, versus testing temperature for niobium containing 2.31 at % oxygen.
Fig. 12 - Influence of temperature on the tensile strength of vanadium containing various amounts of nitrogen. From Thompson and Carlson.

Fig. 13 - Flow stress increment, from 0.5 to 5.0% strain, versus testing temperature for titanium of two purity levels.
Fig. 14 - The microstructure of titanium deformed at $5 \times 10^{-4} \text{s}^{-1}$ and 860 K. Note the evidence of structural instability in this specimen deformed at a temperature above the work hardening peak. R.A. 97%. Magnification 480 times. From Donoso, Santhanum and Reed-Hill.

Fig. 15 - The strain-rate dependence of the reduction in area versus testing temperature curves of commercial purity titanium containing 0.4 at % oxygen. From Donoso, Santhanum and Reed-Hill.
Fig. 16 - The microstructure in the neck region near the fracture surface of a 33\(\mu M\) grain size commercial purity titanium specimen deformed at 5\(\times\)10\(^{-4}\) s\(^{-1}\) and 760 K. At this grain size the structure is stable. Magnification 144 times. From Donoso, Santhanum, and Reed-Hill.

Fig. 17 - The effect of strain-rate on the average work-hardening rate between 0.5 and 5.0\% strain of commercial purity titanium deformed at 760 K. From Donoso, Santhanum and Reed-Hill.
Fig. 18 - The combined flow stress-ductility versus testing temperature curves for Molybdenum-TiM alloy containing 100 wt ppm carbon showing the dependence on the strain-rate. From Wilcox, Gilbert and Allen.
Fig. 19 - Schematic drawing showing a phenomenological description of the intermediate temperature grain boundary cracking mechanism observed in recrystallized Mo-TZM alloys. From Wilcox, Gilbert and Allen.