1963

A study of the strain-aging and brittle-ductile transition characteristics of chromium

Kenneth Edwin Solie

Iowa State University

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A STUDY OF THE STRAIN-AGING AND
BRITTLE-DUCTILE TRANSITION CHARACTERISTICS OF CHROMIUM

by

Kenneth Edwin Solie

A Dissertation Submitted to the
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Approved:

In Charge of Major Work

Head of Major Department

Dean of Graduate College

Iowa State University
Of Science and Technology
Ames, Iowa

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I. INTRODUCTION

The need for materials which are capable of operating at elevated temperatures in oxidizing atmospheres has become increasingly critical in recent years. Applications in the nuclear, missile and space industries are presently demanding materials which will function at temperatures in the order of 2000°F. To date, the complex nickel and cobalt base superalloys are the only materials that approach meeting the necessary specifications.

In the early 1950's considerable hope was held for refractory metals, such as molybdenum and niobium, to replace these superalloys. However, the extreme reactivity of the refractory metals has presented a problem. These metals have been generally successful only in applications where a highly individual coating could be employed.

Chromium possesses the necessary attributes of oxidation resistance and high temperature strength which are necessary for use under these conditions. The development of chromium and chromium-base alloys, however, has been plagued by serious ductility problems. These problems result in fabrication difficulties at ambient temperatures and design problems associated with this general lack of ductility.
Recent studies have indicated that several of the disadvantages in the use of chromium as a high temperature material result, at least in part, from the presence of interstitial impurities. Since, at the present time, greater purification on a production level is impractical, other techniques must be found to minimize the effect of these impurities. In order to determine the necessary techniques, it is desirable to have a knowledge of the basic mechanisms by which these interstitials produce the observed effects.

Of the interstitials that commonly occur as impurities in chromium, numerous investigations have indicated that nitrogen is directly responsible for several of the undesirable effects observed. In addition, nitrogen is known to affect the transition temperature in an anomalous manner, increasing the ductility transition in some conditions of heat treatment and leaving it unaltered in others. For these reasons nitrogen has been singled out as the interstitial of primary concern in this investigation.

It is the intent of this study, therefore, to determine experimentally the effect of nitrogen on the plastic behavior and brittle-ductile transition of chromium and to relate these observations to current theories. Through a study of
the high temperature mechanical behavior and the return-of-yield point characteristics, it is hoped that a clearer picture of the mechanisms by which nitrogen produces the observed strain-aging effects will be obtained.

By investigating the effect of nitrogen in various concentrations and states of distribution on the transition temperature of single and polycrystalline chromium, it will be possible to evaluate the relative effects of grain boundaries and impurities on the brittle-ductile transition. These results will be interpreted on the basis of existing theories, and it is hoped that a clearer concept of the overall effect of these variables can be presented.
II. REVIEW AND ANALYSIS OF LITERATURE

A literature survey was conducted with the objective of obtaining a comprehensive outline of previous experimental data and theories which pertain to the mechanical behavior of body-centered-cubic metals. Emphasis has been placed on the strain-aging and brittle-ductile transition behavior of these materials.

In this discussion it will be assumed that the reader is familiar with the basic theories of the mechanical behavior of materials. These concepts will be discussed only as they relate to the mechanical phenomenon of interest in this study.

The information obtained from this survey will be utilized to assist in understanding the experimental data gathered during the course of the investigation. Direct comparison of these data with that of other investigators and correlation of the experimental results with existing theories will be made where possible.

A. Interactions of Impurity Atoms and Dislocations

The concept of dislocation-impurity atom interactions is of considerable importance in the understanding of both
types of mechanical behavior of concern in this investigation. A general discussion of the process by which solute atoms are segregated to dislocations in body-centered-cubic metals, and the overall effects of such a segregation will be presented here. The specific manner in which this phenomenon can be utilized to explain the experimental observations will be discussed where appropriate.

Elastic (1), electrical (2), chemical (3), and geometrical (4) interactions have been postulated as mechanisms responsible for the segregation of solutes to dislocations. Of these, it appears that the elastic interaction is the most important. Cottrell (5) has estimated the force of this interaction to be several times stronger than the others proposed. In his model Cottrell has assumed that the elastic stresses introduced into the lattice by an edge dislocation can be relieved by the migration of both substitutional and interstitial solute atoms to the stressed regions. Large atoms are gathered to the dilated region of the dislocation field and small ones to the compressed region. He has derived an expression (6) predicting the number of solute atoms per unit volume, \( n(t) \), which can be segregated to a stationary dislocation after a time, \( t \), at temperature, \( T \), is given by:
\[ n(t) = n_0L \propto \left( \frac{ADt}{kT} \right)^{2/3}. \] (1)

Here, \( n_0 \) is the solute concentration at zero time; \( D \), the diffusion coefficient of the solute; \( L \), the total length of dislocation per unit volume; \( \propto \), a numerical constant; and \( A \), a constant that depends on the strain introduced by the solute atoms. Harper (7) has modified Cottrell's original theory by suggesting that the driving force for segregation decreases as the "atmosphere" is formed, and the rate of removal of solute atoms is proportional to the concentration left in solution at any instant. Defining \( q = n(t)/n_0 \), he postulates that aging should follow an equation of the form:

\[ \frac{dq}{dt} = (1-q) \propto L \left( \frac{ADt}{kT} \right)^{2/3}. \] (2)

Nabarro (8) has calculated the tetragonal distortion produced by an interstitial atom in a body-centered-cubic lattice and shown that these atoms can interact with screw as well as edge dislocations.

It is interesting to note at this point that this segregation of solute atoms to dislocation has been observed electron microscopically by Weissmann (9). He states that the existence of an interstitial in the stress field of a dislocation increases the rate of etching in the region of the impurity atom and results in an abnormally thin metal
foil. The interstitials then appear as lighter spots along the dislocation line in his transmission electron micrographs, and these micrographs serve as strong supporting evidence for the concept of the segregation of interstitial atoms to dislocations.

The most dramatic result of this segregation is the existence of the yield point. Cottrell (10) has suggested that the "atmosphere" formed effectively locks the dislocation in place by reducing the strain energy around it. In order for deformation to occur sufficient stress must be applied to remove the dislocation from this energetically favorable position. Once removed from its pinning atmosphere, however, the unlocked dislocation will pass more easily through the lattice with an accompanying decrease in applied stress and the observation of a yield point.

The observed temperature dependency of the yield strength can also be explained on the basis of this model. Thermal energy, available to help the dislocation out of the energy depression created by the atmosphere, decreases rapidly with decreasing temperature. A greater applied stress is necessary to move the dislocation, and the observed increase in yield strength results.
As these examples show, dislocation pinning has a broad effect on the deformation characteristics of a metal. Additional examples of this will be brought out in future discussions.

It should be noted that recent studies have shown that Cottrell locking does not completely explain the observed temperature dependency of the yield strength. Several investigators (11, 12) have attempted to modify Cottrell's theory to include the Peierls-Nabarro lattice frictional force. However, since Cottrell locking is the mechanism of prime concern here, extensions of this theory are left to the reader.

B. The Solubility, Diffusion, and Precipitation of Interstitials in Chromium

The literature contains little information on the solubility of interstitials in chromium. From the information available, however, Hahn et al. (13) have estimated the interstitial content likely to be maintained in solid solution after moderate cooling for several of the refractory metals. This estimate is based on a calculation of the equilibrium solubility at the temperatures where $D = 10^{-11}$ cm$^2$ per sec. At lower temperatures the remaining interstitial atoms are
assumed to be frozen into solution. A summary of these data is presented in Table 1.

Table 1. Effective interstitial solubility of the refractory metals after moderate cooling rates (ppm of interstitial)

<table>
<thead>
<tr>
<th>Metal</th>
<th>H</th>
<th>C</th>
<th>N</th>
<th>O</th>
</tr>
</thead>
<tbody>
<tr>
<td>V</td>
<td>10,000</td>
<td>1000</td>
<td>5000</td>
<td>3000</td>
</tr>
<tr>
<td>Nb</td>
<td>9,000</td>
<td>100</td>
<td>300</td>
<td>1000</td>
</tr>
<tr>
<td>Ta</td>
<td>4,000</td>
<td>70</td>
<td>1000</td>
<td>200</td>
</tr>
<tr>
<td>Cr</td>
<td>0.1-1</td>
<td>0.1-1</td>
<td>0.1</td>
<td>0.1</td>
</tr>
<tr>
<td>Mo</td>
<td>0.1</td>
<td>0.1-1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>W</td>
<td>not detectable</td>
<td>&lt;&lt;0.0</td>
<td>&lt;&lt;0.1</td>
<td>1</td>
</tr>
</tbody>
</table>

For the most part, information on the diffusion of interstitials in chromium is also unavailable. Recently however, Weaver (14) and de Morton (15) have studied the diffusion of nitrogen in chromium and suggested values for its activation energy. Weaver has followed the kinetics of the precipitation of chromium nitride from quenched solid solutions through measurement of the change in resistivity occurring on aging. These data are shown in Fig. 1. Assuming that the rate of precipitation is controlled by the diffusion of nitrogen to the growing particles, he has calculated activation energies for the diffusion of nitrogen in chromium from his data and found values ranging from 17.8
Fig. 1. Decrease in the electrical resistivity occurring on aging of quenched chromium-nitrogen solid solutions according to Weaver (14)
to 25.7 kcal/mole. It can be noted from the data in Fig. 1 that the total change in resistivity during precipitation decreases with decreasing aging temperature. Since a finer precipitate is formed at a lower aging temperature, it appears that the residual resistivity effect of the precipitate is greater the finer the precipitate dispersion. Through internal friction studies, de Morton has found the diffusion of nitrogen in chromium to be predicted by the equation:

$$D = 3.0 \times 10^{-4} \exp \left( \frac{-24,000}{RT} \right).$$  \hspace{1cm} (3)

This activation energy is in good agreement with that determined by Weaver.

Peterson (16), in a recent review of diffusion in refractory metals, has suggested an activation energy of 26,500 cal/mole for carbon in chromium. He cautions, however, that this value is unverified and of doubtful reliability.

**C. Strain-Aging**

For the purpose of definition strain-aging can be classified as either static or dynamic. A typical example of the first type is the return-of-yield point observed after interruption of a strength test. The second type occurs during dynamic straining in a normal tensile test and is characterized by an abnormal temperature dependency of the mechanical
1. Experimental observations

Lubahn (17) has suggested that strain-aging produces four mechanical effects. These are:

1. A maximum in the ultimate tensile strength versus temperature curve.
2. A minimum in the strain rate sensitivity versus temperature curve.
3. Discontinuous yielding.
4. Return-of-yield point after straining and aging.

Hundy (18) and others have noted an additional effect associated with the return-of-yield point phenomenon. They have observed that aging for times longer than those required to produce the yield-point-return frequently results in an increase in the flow curve as well. This effect has been termed strain-age hardening. Typical examples of each of these characteristics are shown in Fig. 2.

Strain-aging was first observed in mild steel and, for many years, it was thought that the phenomenon was peculiar to this material. It is now apparent, however, that strain-aging is much more widespread than first supposed, effecting in some way the mechanical behavior of most of our commercial metals. For example, at least one of the strain-aging char-
Fig. 2. Typical examples of the mechanical effects associated with strain-aging
A. Maximum in UTS with temperature

B. Minimum in strain-rate sensitivity with temperature

C. Discontinuous yielding

D. Return of yield point
acteristics has been noted in all of the body-centered-cubic metals (19-23) and in many face-centered-cubic and hexagonal close packed materials (24-28, 17). A comprehensive summary of the subject of strain-aging in refractory metals has been presented by Imgram (29).

The high temperature mechanical behavior and strain-aging characteristics of chromium have been the subject of numerous investigations during recent years. Pugh (30) has tested chromium in tension and noted peaks in the yield strength, ultimate tensile strength, and strain-hardening exponent versus temperature curves at 450°C.

In agreement with these results, Johansen et al. (31) have detected a maximum point in the ultimate tensile strength and minimum points in the reduction-in-area and elongation curves of chromium at 500°C.

Metcalfe et al. (32) have noted discontinuous yielding to be prevalent below 550°C and also observed a maximum in the ultimate tensile strength at this temperature. They also noted a low strain rate sensitivity at 425 and 550°C. Marcinkowski and Lipsitt (33) have carried out compressive tests on chromium between -200 and +400°C and found a strain-aging peak at 300°C.
It is of interest to note at this point that strain-aging peaks appear to occur in two temperature regions, the lower one at about 300°C and the higher one between 450-550°C. From this observation the existence of two strain-aging peaks seems a possibility. Weaver (34) has verified this occurrence in chromium, tested in tension at a strain rate of $8.3 \times 10^{-3} \text{ min}^{-1}$. These data are reproduced in Fig. 3. His results clearly show the existence of peaks at approximately 400 and 600°C in a material containing 0.002% nitrogen and maxima at 300 and 400°C in chromium with 0.0005% nitrogen. It appears from these data that increasing the nitrogen concentration from 0.0005 to 0.002% has shifted the 300°C peak to 600°C while leaving the 400°C peak unchanged. Evidence has been presented by Schmidt et al. (35) that two peaks also exist in the ultimate tensile strength versus temperature curve in tantalum.

Only a limited amount of data is available in the literature regarding the return-of-yield point phenomenon in chromium. Marcinkowski and Lipsitt (33) have shown that there is a reoccurrence of the yield point even after immediate reloading at 200°C. Additional aging up to one hour seems to have increased the flow stress of the specimen.
Fig. 3. Ultimate tensile strength versus temperature for chromium containing 0.0005 and 0.002 percent nitrogen according to Weaver (34).

Fig. 4. Examples of the return-of-yield point in chromium as observed by Marcinkowski (33).
in addition to producing a return-of-yield point. Examples of these results are illustrated in Fig. 4. Weaver (36) has also found direct evidence of strain-aging in chromium by repeatedly straining the metal just beyond its yield point. The yield point was observed to return after initial straining, and the flow stress rose appreciable above the preceding maximum applied stress. It is presumed that the mechanism responsible for the increase in flow stress observed by these investigators is similar to that proposed by Hundy (18) for the effect of mild steel.

While it is accepted that interstitial solute atoms are responsible for the observed strain-aging effects in body-centered-cubic metals, little has been done to determine the specific impurity acting in the case of chromium. Metcalfe et al. (32) have studied a chromium-0.7 per cent titanium alloy and observed that titanium effectively removed nitrogen from free solution. In addition, they noted that strain-aging effects were reduced in this alloy. This indicates that nitrogen is responsible, at least in part, for the existence of strain-aging in chromium. In agreement with this observation Wain et al. (37) and Weaver (34) have suggested that, of the interstitials in solid solution in
chromium, nitrogen has the most powerful effect on the mechanical properties.

2. Discussion of observations in terms of current theories

The phenomenon of yield-point-return after prestraining and subsequent aging has been recognized for many years. Until Cottrell's suggestion of solute atom segregation, however, no satisfactory mechanism for such a process had been put forth. Cottrell noted that when a body-centered-cubic metal is slowly cooled following recrystallization, the dislocations present are surrounded by an impurity cloud formed by the mechanism described in Section A. If this metal is then deformed, free dislocations are reintroduced into the lattice through unlocking of existing defects or generation of fresh ones. Cottrell and Bilby (6) have suggested that if the metal is aged subsequent to this straining, relocking of the dislocations can occur, and the return-of-yield point is observed.

On the basis of this model Cottrell and Bilby have predicted and verified experimentally that the time to the 2/3 power dependence shown in Equation (1) for initial solute segregation should also hold for the rate of yield-point-return, since the magnitude of the yield point is a direct
function of the amount of interstitial segregated to the dislocation. Bullough and Newman (38), however, have also considered the flow of impurities to a dislocation, making allowance for core saturation due to back diffusion and depletion. They arrive at a \( t^{2/3} \) dependence for initial aging in agreement with Cottrell and Bilby. At longer times, however, they predict that a steady state is reached, and the rate of solute segregation should level off. Thomas and Leak (39) and others (7, 40) have calculated the density of these atmospheres from return-of-yield point data and have obtained values ranging from 6 to 118 solute atoms per atom plane of dislocation. These values are much higher than those originally proposed by Cottrell. Thomas and Leak also note that the \( t^{2/3} \) law is valid far beyond the predicted saturation point of the dislocation. Dahl and Lücke (40) and Bilby and Leak (41) have suggested that precipitation must be occurring on the dislocation to cause such absorption. Precipitation of this type would enable the dislocations to continue to act as sinks for solute atoms and allow the continuation of the \( t^{2/3} \) dependence.

Hundy (18) was the first to propose that this precipitation was actually occurring and experimentally show that it
resulted in the strain-age hardening effect. He reasoned that once the dislocation is freed from its atmosphere, the remaining interstitial cloud should exhibit no further influence on the dislocation's motion. Therefore, the dislocation locking mechanism suggested by Cottrell is unable to account for the observed increase in flow stress after aging. Considering his observations then, Huridy concluded that hardening, resulting from precipitation on the dislocations as described above, must be responsible for the observed increase in flow stress.

This proposal has led to a detailed study of the phenomenon of precipitation on dislocation. Wilson and Russell (42, 43) have investigated the individual contributions of dislocation locking and precipitation to the strain-aging of low carbon steel. They conclude that the increase in the lower yield strength is first due to dislocations locking; however, after longer aging times precipitation accounts for the continued increase. Doremus et al. (44-46) have studied the precipitation of carbides in strain-aged iron, electron microscopically, and claim to have observed their formation on dislocations. Leslie and Keh (47), however, have looked for these precipitates using transmission techniques and have been unsuccessful in their search.
Discontinuous yielding is a typical example of "dynamic" strain-aging. Serrations have been observed in the tensile curves of metals at both very low temperatures and near or above room temperature. The low temperature discontinuities are a result of twinning and not strain-aging. Ambient temperature serrations, however, have been attributed to locking and unlocking of dislocations during deformation. Cottrell (48) has derived a relationship for the strain-rate effects on repeated yielding based on an empirical analysis of data available for alpha iron. He has shown that at the minimum temperature for repeated yielding, \( \dot{\varepsilon} = 10^9 D \) where \( \dot{\varepsilon} \) is the strain rate, \( D \) is the interstitial diffusivity and \( 10^9 \) is a constant. This constant is dependent on the interstitial concentration and the dislocation-interstitial interaction energy and may not be \( 10^9 \) for metals other than alpha iron. Sleeswyk (49) has recently proposed a somewhat more elaborate locking mechanism to explain observed effects; however the process is not of specific concern in this investigation and will not be discussed here.

At temperatures near those at which discontinuous yielding occurs peaks appear in plots of strength versus temperature, and anomalies are observed in the temperature dependency
of the strain-rate sensitivity and strain-hardening exponent. Nabarro (8) has reasoned that in the temperature range where a strain-aging peak exists, the pinning atmosphere has sufficient mobility to diffuse along with the gliding dislocations, resulting in a "viscous drag" and an increased strength. At higher temperatures the atmosphere becomes so dilute that essentially no locking exists, and at lower temperatures the interstitial atom mobility is so low that the atmosphere cannot move with the dislocation. Nabarro attributed the appearance of more than one strain-aging peak, as has been observed in chromium, to the presence of additional interstitials capable of producing locking. The ability to resolve these peaks is dependent on the difference in mobility of the interstitials involved.

Eccentricities in the strain-rate sensitivity and strain-hardening exponent can also be explained on the basis of dynamic strain-aging. Strain-hardening has been explained by Mott (50) in terms of back stresses exerted on dislocation sources by pile-ups, making further application of stress necessary to continue straining. These back stresses are relieved by vacancy diffusion which enhances dislocation climb around barriers. Cottrell atmospheres impede this relief in the strain-hardening exponent.
The temperature dependency of the strain-rate sensitivity is also related to the self-diffusion process which, as indicated above, decreases the flow stress through vacancy migration to pile-ups. With increasing strain rates the likelihood of this type of stress relief is lessened, and this difference in the probability of stress relief between faster and slower strain-rates becomes more pronounced at higher temperatures. Since the strain-rate sensitivity ($n$) is defined as $\log \frac{\sigma_2}{\sigma_1}$, it is apparent that if $\sigma_2$ is increasing more rapidly than $\sigma_1$ with temperature a progressively increasing rate sensitivity results. In the strain-aging region, however, dislocation atmospheres impede the stress relief process, the divergence of $\sigma_2$ and $\sigma_1$ is lessened, and a lowered strain-rate sensitivity results.

3. The effect of strain-aging on the electrical resistivity

In addition to the effects of strain-aging on the mechanical behavior of materials it has also been noted that other properties such as hardness, impact strength, and internal friction can be influenced by this phenomenon.

It has been suggested (51) that, if the Cottrell mechanism for the description of strain-aging is correct, the electrical resistivity of the material would be expected to
decrease during aging. This decrease in resistivity should result from a migration of solute atoms from random solution to some other arrangement, presumably dislocation atmospheres in which they are less effective in scattering electrons. Dijkstra (52) has shown that complete removal of 0.1 weight per cent solute from the alloy causes a 2.5% change in resistance for carbon and a 3.5% change for nitrogen in iron.

Segregation of interstitials to dislocations should be much less effective than removal in reducing the resistivity but, none-the-less, would be expected to give a similar though smaller change.

Cottrell and Churchman (51) and Dahl and Lücke (40) have found this effect experimentally. Cottrell observed a 0.2% difference in the resistivity after aging of a strained iron wire. By aging these strained wires at several different temperatures Cottrell was able to determine that this change in resistivity exhibited the same characteristics as the yield-point-return, thus verifying that the same mechanism is responsible for both effects.

Since the contribution of these interstitials to the resistivity is temperature independent, it was thought advisable to follow the procedure of Krautz and Schultz (53) and
measure the ratio of the resistivities at room temperature and 4.2°K, thus reducing the thermal contribution to the resistivity and enhancing the influence of point defects.

D. Brittle-Ductile Transition

The occurrence of a brittle-to-ductile transition in metals has been recognized for many years. This ductility transition results in an abrupt change from brittle behavior to ductile behavior over a very narrow temperature range. The phenomenon is most pronounced in the body-centered-cubic metals of Groups Va and VIA. It has, however, been observed in several metals with close-packed structures (54, 55).

1. Experimental observations in body-centered-cubic metals

A summary of the brittle-ductile transition characteristics of refractory metals has been presented by Schwartzberg, Ogden, and Jaffee (56). With the exception of tantalum, all of the refractory metals in Group Va and VIA exhibit a brittle-to-ductile transition. Comparative values of the transition temperature of several of these refractory metals and iron are shown in Table 2.

Much of the past research in the area of ductility transitions has concerned itself with the effects of interstitial solutes on the transition temperature. These
studies have shown that interstitials can cause a large increase in the transition temperature and have led some investigators to believe that the occurrence of the ductility transition is a result of these impurities. A comprehensive summary of the influence of interstitials on the ductility transition has been presented by Hahn, Gilbert, and Jaffee (13) and will not be reviewed here.

Table 2. Typical values of the tensile transition temperature for several body-centered-cubic metals

<table>
<thead>
<tr>
<th>Metal</th>
<th>Transition temperature °C</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>W</td>
<td>200</td>
<td>Bechtold and Shewmon (23)</td>
</tr>
<tr>
<td>Mo</td>
<td>0</td>
<td>Bechtold and Scott (57)</td>
</tr>
<tr>
<td>V</td>
<td>-100</td>
<td>Clough and Pavlovic (58)</td>
</tr>
<tr>
<td>Nb</td>
<td>-125</td>
<td>Wessel (59)</td>
</tr>
<tr>
<td>Fe</td>
<td>-150</td>
<td>Geil and Carwile (60)</td>
</tr>
</tbody>
</table>

The recent resurgence of interest in chromium as a refractory material has prompted a number of investigators to study various aspects of its ductility transition. A
Table 3. A summary of recent data concerning the effect of interstitials on the brittle-ductile transition temperature in chromium

<table>
<thead>
<tr>
<th>Interstitial content</th>
<th>Transition temperature °C</th>
<th>Reference</th>
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<tbody>
<tr>
<td></td>
<td>wrought</td>
<td>recrystallized</td>
</tr>
<tr>
<td>75 ppm</td>
<td>-15</td>
<td>300</td>
</tr>
<tr>
<td>180 ppm (O)*</td>
<td>25</td>
<td>400</td>
</tr>
<tr>
<td>625 ppm (O)*</td>
<td>30</td>
<td>390</td>
</tr>
<tr>
<td>175 ppm (N)*</td>
<td>160</td>
<td>290</td>
</tr>
<tr>
<td>180 ppm (C)*</td>
<td>150</td>
<td>470</td>
</tr>
<tr>
<td>0.026% N</td>
<td>137</td>
<td>-</td>
</tr>
<tr>
<td>1.0% N</td>
<td>260</td>
<td>-</td>
</tr>
<tr>
<td>0.002% N</td>
<td>-</td>
<td>380</td>
</tr>
<tr>
<td>0.03% N</td>
<td>-</td>
<td>350</td>
</tr>
<tr>
<td>0.01% N</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>0.5% N</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>0.008% N</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>0.015% N</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>0.0005% N</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>0.0012% N</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

*Principle impurity as indicated.
summary of the influence of interstitials on the brittle-ductile transition temperature in chromium is presented in Table 3. Several conclusions can be drawn from these data. Carbon appears to increase the transition temperature under all conditions of heat treatment studied, while oxygen shows no observable effect. However, nitrogen behaves in an inconsistent manner. In the wrought condition the transition temperature shows a marked nitrogen concentration dependence. In the recrystallized and slow-cooled condition nitrogen apparently has little or no effect. Quenching after recrystallization, however, causes a drastic increase in transition temperature and again introduces a nitrogen dependency. This behavior indicates that the transition temperature of chromium is dependent not only on the nitrogen concentration but also on the distribution in the metal. Additional data showing the influence of impurity distribution has been described by Wilms and Rea (65) who have also observed a sharp increase in the transition temperature with increasing cooling rate.

Hook and Adair (66) among others (67, 68) have investi-
gated the ductility transition characteristics of recrystallized chromium and have observed anomalous behavior of the transition temperature with grain size. In most materials exhibiting a brittle-ductile transition temperature, increasingly finer grain sizes produce a progressive increase in the ductility transition. Hook and Adair observed that the transition temperature of chromium with a specific grain size varied with sample diameter. Noting this, they have postulated that the transition temperature is not dependent on the grain size directly, but rather on a parameter termed the size factor, \( S \). This size factor is defined to be the ratio of the specimen diameter to the average planer grain size. Their data then shows that the transition temperature decreases with decreasing sample size or increasing grain size, both of which result in a lower value of the size factor.

These investigators have also found that prestraining chromium above its original ductility transition results in a large decrease in the transition temperature. Hook and Adair observed this rheotropic recovery to be greater than 150°C after a prestrain of 4% carried out just above the
initial ductility transition.

In agreement with the above investigators McNeil and Limb (69) and Hook, Adair and Lipsitt (70) have observed the brittle fracture of chromium to initiate at or near grain boundaries. Hook et al. (70) have proposed intergranular rupture occurring at the intersection of slip bands and grain boundaries to be the initiating mechanism. However, McNeil and Limb suggest cleavage on the (100) planes to be responsible.

2. Theoretical considerations

While a firm theoretical explanation for the existence of a ductility transition in metals has been difficult to visualize, several suggestions have been presented which qualitatively explain the experimental observations. It has been noted that the ductility transition usually occurs in the temperature region where the yield strength is rapidly increasing. With decreasing temperature the yield strength increases more rapidly than the fracture strength, and brittle failure occurs when the first exceeds the latter. Wessel (71) has proposed a mechanism explaining this behavior. He suggests that above the transition temperature, a sufficient number of the initially locked dislocations are released at
a rather low stress and move through the lattice prior to the sharp yielding. This dislocation motion results in the observed preyield microstrain. These freed dislocations pile up as barriers, and when a critical concentration is reached, they break away simultaneously producing the observed yield point.

At subtransition temperatures the mechanism is slightly different. At these low temperatures high stresses, due to Cottrell locking, are required to cause dislocation motion. Some of the localized stresses produced in this manner are sufficiently high to exceed the fracture stress and initiate small cracks. The propagation of these cracks to cause brittle failure then depends on the relative rates of crack growth and normal yielding.

Two basic mechanisms of brittle fracture are currently popular. Both of these require the motion of dislocation, i.e. preyield plastic strain, before brittle fracture can occur. Cottrell pictures the most difficult process in fracture to be the growth of a crack nucleus, whereas Stroh believes the controlling phase to be crack nucleation. Stroh (72) in agreement with an earlier postulate by Zener (73) has suggested that under certain conditions, it is energetically favorable for a dislocation pile-up, formed at a barrier, to
coalesce to form a crack. He arrived at the following equation describing the fracture stress, $\sigma_f$:

$$\sigma_f = \sigma_1 + kd^{-\frac{1}{2}}.$$ 

In this equation $\sigma_1$ is a frictional stress necessary for correlation with experimental data; $k$ is a constant containing Poisson's ratio, the crack surface energy, and the shear modulus; and $d$ is the grain diameter. Stroh then states that if this coalescence occurs, brittle fracture results. If, however, the pile-up subsequently yields, ductile behavior is observed.

Cottrell (74) suggests that crack nuclei can form at the junction of two glide planes and through the coalescence of slip dislocations into cleavage dislocations. The propagation of the crack is then dependent on the continued forcing of slip dislocations into the crack embryo. Thus if the yield strength is less than the back stress set up at the point of coalescence, the crack does not grow and ductile behavior is expected. If, however, the yield strength is higher than this back stress, the crack growth is more favorable and brittle fracture is observed.

Several different mechanisms have been suggested to explain the experimentally observed brittleness in chromium.
Wain et al. (62) and Weaver and Gross (75) have both considered crack propagation to be the controlling factor. They assume the existence of a crack produced by one of the above mechanisms and suggest that subsequent behavior of this crack is governed by the properties of dislocation sources near the tip. These sources, operating under the influence of the shear stresses developed at the crack tip, cause dislocation motion across the path of the crack. This plastic deformation leads to a blunting of the sharp crack and a reduction in the strain energy in the vicinity of the crack both of which reduce the speed of crack propagation. Any factor which raises the stress necessary for the initiation of these secondary sources is likely to increase the tendency toward brittleness. Wain and Weaver have considered Cottrell locking and precipitate-dislocation interactions to be two such inhibiting processes. The combined effect of these hindrances has been summarized by Weaver and Gross in the following manner. Near the crack tip, a number of dislocation sources are available to produce plastic flow. While Cottrell locking renders some of these sources inoperative, the shear stresses introduced by the propagating crack cause isolated dislocation avalanches. The movement of dislocations from
these sources across the path of the crack is inhibited by the precipitate particles due to the back stress induced by formation of dislocation loops around the barriers. The terminal velocity of the propagating crack is then controlled by the amount of slip occurring. With the presence of precipitates the advance of the crack is delayed to some extent but not stopped as would be the case if plastic deformation could take place readily around the tip of the crack.

On the other hand, Hook and Adair (66) propose that crack initiation is the controlling process. They feel that the probability of grain boundary initiated fracture is the most important factor in determining the brittle-ductile transition. On the basis of their data regarding the relative effect of sample size and grain diameter on the transition temperature, they have concluded that fracture in chromium is initiated by grain boundary rupture resulting from dislocation pile-up. They attribute the occurrence of rheotropic recovery in chromium to the generation of dislocation paths through the grain boundaries during prestraining above the transition temperature. These paths then reduce the probability of dislocation pile-up at lower temperatures, and stress concentrations sufficient to nucleate cracks are
McNeil and Limb (69) agree that fracture is initiated at grain boundaries. Their observations, however, indicated that cleavage on the (100) planes at or near the boundaries is the responsible mechanism.
III. SAMPLE PREPARATION

Fabrication of the base chromium and chromium-nitrogen alloys into a form from which suitable test specimens could be machined required considerable development effort. After investigating a number of different techniques, the following procedures were found to produce adequate specimens with good reliability and were used throughout the investigation.

A. Materials

Iodide chromium, obtained in crystal form from the Chromalloy Corporation, was used as the base material in this investigation. The initial step in the preparation of the test specimens consisted of arc-melting the chromium crystals into ingots measuring approximately 6 in. long by \( \frac{1}{2} \) in. in diameter. Arc-melting was carried out under an atmosphere of argon in a water-cooled copper hearth. Impurities in the argon were "gettered" by melting a zirconium button prior to each chromium melt. A typical analysis of the base material before and after arc-melting is given in Table 4.

The technique employed for the introduction of nitrogen into the test alloys depended on the intended use of the alloy. For the preparation of the nitrogen alloy for tensile specimens, the interstitial was introduced by an alloy addition technique. A master alloy was prepared by arc-melting
iodide chromium under a 50% nitrogen, 50% argon atmosphere. Nitrogen was continually charged to the chamber as a decrease in the pressure showed it was being taken up by the chromium. This master alloy was sectioned and remelted three times in the absence of nitrogen to produce a homogeneous alloy. Analysis showed the master alloy to contain 2.10 weight percent nitrogen. The amount of alloy needed to give the desired nitrogen concentration was then calculated and added to iodide chromium to produce the test alloy. This test alloy was then homogenized as described above and melted into ingots for future forming. It was found that this alloy could be successfully swaged into rods suitable for the preparation of the tensile specimens.

Table 4. Typical analysis of the base chromium before and after arc-melting

<table>
<thead>
<tr>
<th>Element</th>
<th>Ppm before arc-melting</th>
<th>Ppm after arc-melting</th>
</tr>
</thead>
<tbody>
<tr>
<td>O</td>
<td>25</td>
<td>40</td>
</tr>
<tr>
<td>H</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>N</td>
<td>10</td>
<td>30</td>
</tr>
<tr>
<td>C</td>
<td>45</td>
<td>50</td>
</tr>
<tr>
<td>Al</td>
<td>3</td>
<td>--</td>
</tr>
<tr>
<td>Ca</td>
<td>1</td>
<td>--</td>
</tr>
<tr>
<td>Fe</td>
<td>50</td>
<td>50</td>
</tr>
<tr>
<td>Mg</td>
<td>1</td>
<td>--</td>
</tr>
<tr>
<td>Cu</td>
<td>1</td>
<td>--</td>
</tr>
<tr>
<td>Mn</td>
<td>1</td>
<td>--</td>
</tr>
<tr>
<td>Mo</td>
<td>1</td>
<td>--</td>
</tr>
<tr>
<td>Si</td>
<td>20</td>
<td>--</td>
</tr>
<tr>
<td>Ni</td>
<td>2</td>
<td>--</td>
</tr>
<tr>
<td>V</td>
<td>2</td>
<td>--</td>
</tr>
</tbody>
</table>
Because of the edge cracking observed in attempting to roll rods prepared in this manner into strip and the difficulty encountered in producing single crystals of nitrogen alloys, a thermal charging technique was employed to introduce nitrogen into the bend samples. In this procedure test samples produced, as described below, from the pure chromium were heated for three hours at temperatures ranging from 1000 to 1200°C under nitrogen at a pressure of 760 mm of Hg. After charging, the nitrogen atmosphere was replaced by argon, and the samples were homogenized for 24 hours at the charging temperature. Nominal nitrogen concentrations were checked by chemical analysis of the samples after testing.

B. Bend Specimens

Both single crystal and polycrystalline bend specimens were utilized in this study and were prepared by the following techniques.

1. **Polycrystalline samples**

Arc-melted ingots of iodide chromium were jacketed in mild steel and swaged at a furnace temperature of 800°C into 3/8 in. diameter rods. These rods were then rolled at a furnace temperature of 500°C into strip about \( \frac{1}{2} \) in. wide by 0.070 in. thick. Specimens measuring 1 in. x \( \frac{1}{2} \) in. were cut
from this strip and surface ground to a thickness of 0.055 in. If nitrogen alloys were desired, these samples were charged and recrystallized as described above. Pure chromium samples were recrystallized at 1000°C in a vacuum of approximately 10^{-6} mm of Hg for one hour. All samples were furnace-cooled at a rate of 200°C per hour or oil quenched subsequent to these thermal treatments. Analysis showed no appreciable pick-up of any other interstitial impurities during the recrystallization or nitrogen charging operations.

Following these procedures the samples were brought to a final thickness of 0.040 in. by electropolishing using orthophosphoric acid as the electrolyte and a current of 15 amps at 15 volts. The temperature of the electrolyte was maintained at 60 to 70°C during polishing. This technique produced a bright mirror-like finish on the specimens.

2. Single crystal samples

Arc-zone refining was utilized to produce single crystals of chromium from the arc-melted ingots for the preparation of the single grained bend specimens. A schematic diagram of the zone refining apparatus is shown in Fig. 5. The crystal growth was carried out under a zirconium gettered argon atmosphere. A current of 140 amps at 15 volts was employed, and the ingot was drawn under the arc at a speed of \( \frac{1}{2} \) in.
Fig. 5. Schematic diagram of the arc zone-refining apparatus used for the preparation of chromium single crystals
WATER COOLED STAINLESS STEEL ELECTRODE

TO VACUUM AND ARGON GAS

WATER COOLED COPPER HEARTH

WATER COOLED CHAMBER

WATER FLOW

RACK, PINION AND BODINE MOTOR

44
per hour. This technique produced a single crystal region in the center of the arc-melted finger measuring approximately $\frac{3}{4}$ in. in diameter and 3 to 4 in. long. Usable single crystals were obtained in about 90% of the attempts. Bend samples were cut longitudinally from these crystals and machined to the desired size by surface grinding. These samples were then charged or vacuum annealed as described above and electropolished to final thickness.

C. Tensile Specimens

Arc-melted ingots of pure chromium or the nitrogen alloy were jacketed in mild steel and swaged into 3/8 in. diameter rod at a nominal furnace temperature of 800°C. Standard ASTM tensile specimens with a 1/8 in. reduced section (see Fig. 6) were machined from these rods using a precision lathe and carbide cutting tools. Because of the extreme notch sensitivity exhibited by chromium, it was impossible to make gauge markings on the specimens; therefore the gauge length has been taken to be that of the reduced section. Following machining, the samples were electropolished to a bright finish using a circular cathode and revolving the specimen at approximately 10 rpm during the process. The electrolyte and power setting were similar to those employed above.
Fig. 6. Standard ASTM tensile specimen used in all tensile tests
Following polishing the tensile specimens were recrystallized at a temperature of 1000°C for one hour under a vacuum of less than $10^{-6}$ mm of Hg. This technique produced a completely recrystallized structure with a grain size of approximately 20-25 grains/mm$^2$. Recrystallization was confirmed by Laue back-reflection X-ray studies.
IV. EXPERIMENTAL TECHNIQUES AND EQUIPMENT

There are a number of tests available for evaluation of the mechanical properties of a material. Typical tests for the determination of the ductility transition are impact tests, of both the pendulum and falling-weight types, bend tests, tensile and torsion tests. For the investigation in the ductile region tensile and torsional testing are most common, while compression and slow bend tests are occasionally utilized.

The ductility transitions in this investigation were determined by the use of a slow bend test primarily because of the ease of sample preparation and minimum waste encountered in obtaining test specimens.

Tensile tests were employed for the determination of the elevated temperature properties for two reasons. First, the equipment for this type of test was readily available and secondly, most previous investigations of chromium have utilized this technique, and thus more meaningful comparisons are possible.

A. Bend Tests

All bend tests were carried out in a three point loading apparatus of the type used by Sully, Brandes, and Mitchell
(76). This equipment is illustrated schematically in Figs. 7 and 8. High temperatures were obtained by a resistance furnace surrounding the test equipment as shown in Fig. 7. For sub-ambient testing the apparatus shown in Fig. 8 was substituted for the furnace, and low temperatures were obtained by circulating a regulated flow of liquid nitrogen through the hollow copper supporting block and the double walled chamber. Manual control was employed to obtain and hold test temperatures in both cases.

A plunger and lever arrangement, driven by a Bodine variable speed motor, was employed to bend the test samples around a 1/6 in. radius tip. Deflection of the specimen was followed by a dial gauge which monitored the motion of the plunger.

The samples were tested at a rate of 0.050 in. per min to fracture or a full deflection of 0.250 in. The transition temperature was taken to be the average between the lowest temperature at which the sample deflected greater than 0.200 in. and the highest temperature at which the specimen deflected less than 0.050 in. before fracture. It was usually possible to bracket the transition temperature to within \( \pm 5^\circ \)C by this technique.
Fig. 7. Schematic diagram of the elevated temperature bend testing equipment
BODINE VARIABLE SPEED MOTOR

THERMOCOUPLE

DIAL GAUGE FOR DEFLECTION MEASUREMENT

COUNTER WEIGHT

SPLIT FURNACE

STEEL CYLINDER

STEEL PINS

COPPER SUPPORT BLOCK

THERMOCOUPLE

BEND SAMPLE
Fig. 8. Cooling equipment substituted for the furnace in Fig. 7 for low temperature bend testing
LOW TEMPERATURE EQUIPMENT

DEWAR FLASK

LIQ. N₂

CONTROL VALVES

DOUBLED WALLED CYLINDER

BAKELITE BASE

HOLLOW COPPER SUPPORTING BLOCK

NITROGEN OUTLET

STYROFOAM INSULATION

NITROGEN OUTLET
B. Tensile Tests

All specimens were tested on a Tinius Olson 12,000 Pound Capacity Electromatic Universal Tensile Testing Machine. This machine was equipped with a Bristol XY recorder which made a permanent record of the applied load versus instantaneous elongation. The vertical motion of the moveable cross-head was taken as a measure of elongation. This cross-head motion was measured by a Tinius Olson Deflectometer Type D-2. A schematic diagram of the high temperature testing equipment is shown in Fig. 9. The samples were loaded through spherically seated stainless steel balls to assist in providing axial alignment. These balls were seated in stainless steel adapters which in turn were threaded onto 7/8 in. stainless steel draw bars. The bearing surfaces were frequently repolished and lubricated with an aqueous graphite suspension to insure good operation. Above test temperatures of 200°C the grip and sample area was enclosed in a pair of concentric stainless steel cylinders, as shown in the diagram, and a constant flow of argon under a slight positive pressure was passed through these cylinders to reduce sample contamination. During testing, two chromel-alumel thermocouples were attached to the specimen. These thermocouples indicated the
Fig. 9. Schematic diagram of the equipment for elevated temperature tensile testing
maximum thermal gradient to be less than 3°C along the specimen. A control thermocouple was placed next to the windings of the resistance furnace and connected to a Brown Pyr-O-Vane temperature controller. This arrangement maintained the test temperature to ± 3°C throughout the period of the test.

Standard tensile tests used for determining the variation in mechanical properties with temperature were carried out at strain rates of 0.0093, 0.0149, 0.0455 and 0.133 min⁻¹. These values were accurately determined by measuring the cross-head motion versus time with a precision dial gauge and stop watch and calculated on the basis of the 3/4 in. gauge length used.

Interrupted tensile tests were carried out to study the return-of-yield point phenomenon. In these tests the samples were initially strained 6.67% at a rate of 0.0149 min⁻¹, unloaded, aged and strained an additional 4%. It was found that these 4% restrains could be repeated to approximately 20% total strain without any observable strain dependency. This observation is supported by the fact that, within experimental error, identical aging cycles at different strains produced identical changes in the mechanical properties.
C. Aging Procedures

Aging of the quenched bend specimens and strained tensile specimens was carried out in a 50% KNO₃-NaNO₂ fused salt bath, held at the desired aging temperature. The bath was heated by a resistance furnace surrounding the salt container. The aging temperature was regulated by a Brown Pyr-O-Vane Controller to within ± 1°C. Samples were aged in stainless steel tubes suspended in this salt bath. Although it required approximately 90 sec for the specimens to reach aging temperature, all times are reported as those for which the samples were actually in the bath. Following aging, the samples were removed from the bath and allowed to cool in air to room temperature.

D. Metallographic Techniques

Several different types of metallographic processes were employed to investigate changes occurring in various phases of this study. The techniques used are described below.

1. Fractographs

The sample of interest was mounted on a standard Bausch and Lomb Research Metallograph and photographed using standard photographic techniques or Polaroid photography. Various magnifications were used ranging up to 500X. Polarized
light was found to yield a more distinct image of the fracture surface in most cases, and thus this illumination was employed throughout.

2. **Photomicrographs**

The mounted metallographic samples were initially hand polished through 600 grit paper under water. Fine polishing was done in two stages on a Syntron vibratory polisher. The samples were first treated with Linde A polishing powder on a wax lap and then transferred to a microcloth lap charged with Linde B for the final finish. Samples were etched for one hour with Murakami's Reagent \( [6 \text{ gms} \ K_3\text{Fe(CN)}_6 \text{ and } 10 \text{ gms} \ KOH \text{ in } 100 \text{ ml} \ H_2O] \). Some caution with regard to the time of etching was found to be advisable. Long periods resulted in excessive etch pitting which tended to cover the details of the structure. Again both standard photography and Polaroid techniques were employed.

3. **Electron micrographs**

A number of attempts were made to produce thin chromium foils which could be studied under the electron microscope. Both chemical and electrolytic etching proved unsuccessful, however, and it was decided to utilize replica techniques for the electron micrographic studies. Metallographic specimens
prepared in the manner described above were first vapor plated with boric anhydride to enhance removal of carbon film, shadowed with chromium and plated with graphite to form the replica. The replica was then floated off the specimen on water and picked up on copper grids. An RCA model EMU3 electron microscope operating at 50 KV was utilized to view these replicas. A magnification of 6000X was employed in all cases. Standard photographic techniques were used to record the images.

E. Resistivity Ratio Measurements

During the return-of-yield point studies, a measurement of the resistivity ratio was carried out before and after each aging. While our primary concern was with the value of the resistivity at low temperatures, the ratio of the resistivity at 300°K to that at 4.2°K was actually measured. This eliminated the necessity of precise dimensional measurements of the tensile specimen. To accomplish the resistivity measurements, two electrical leads were securely fastened to each end of the tensile specimen. Current was introduced to the samples through the outside leads, and the voltage drop across the specimen was measured between the inside connections. Current was supplied by a standard 12 volt storage
battery and varied in 0.2 amp intervals from 0 to 1.0 amps by means of a potentiometer. The voltage drop was measured at each current setting by a Kiethley Model 140 millimicro voltmeter. To eliminate junction effects the polarity of the direct current was reversed at each setting, and the voltage drop was taken as the average of that found in each direction. The resistivity was taken to be the average of those obtained at each current setting. Similar readings were obtained at room temperature and under liquid He, and the ratio of the resistances in each case was calculated. Precautions were taken to insure draft free conditions at all of the electrical junctions since thermal effects could introduce considerable variation in the voltages observed.
V. PRESENTATION AND DISCUSSION OF EXPERIMENTAL RESULTS

Considering the variety of information gathered during the course of this investigation, it is felt that a full understanding of these observations would be more easily obtained through an integrated discussion of the results as they are presented.

A. Strain-Aging Characteristics

Evidence gathered by other investigators leaves little doubt that the effects of strain-aging are prevalent in chromium. Data obtained during the course of the investigation are in agreement with these observations, and through this study it has been possible to characterize certain of these strain-aging effects somewhat more clearly.

In keeping with the proposed separation of strain-aging phenomenon into those effects which occur during dynamic straining of the metal and those which appear after aging of an initially strained material, discussion of the strain-aging behavior of chromium will be divided into these dynamic and static characteristics.

1. Dynamic strain-aging effects

A comprehensive study of the mechanical properties of chromium as a function of temperature and strain-rate has
been carried out to determine the dynamic strain-aging characteristics of the material. Of the mechanical properties influenced by the strain-aging process, it was observed that the ultimate tensile strength could be reproduced with the greatest reliability, and thus primary emphasis in this phase of the investigation has been given to this parameter.

Plots of the ultimate tensile strength versus temperature data for three of the strain-rates employed in this study are shown in Figs. 10-12. Each of these curves is characterized by the existence of two strain-aging peaks. The temperatures at which these peaks occur become progressively higher with increasing strain-rate. To assist in correlating these maxima with some existing mechanism, it is helpful to know the activation energy associated with each of these peaks. The strain-rate dependence of the peak temperatures, summarized in Table 5, enable the necessary calculations to be made.

<table>
<thead>
<tr>
<th>Strain-rate</th>
<th>Peak temperature °C</th>
<th>Peak designation</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0093</td>
<td>275</td>
<td>1</td>
</tr>
<tr>
<td>0.0093</td>
<td>372</td>
<td>2</td>
</tr>
<tr>
<td>0.0149</td>
<td>305</td>
<td>3</td>
</tr>
<tr>
<td>0.0149</td>
<td>410</td>
<td>4</td>
</tr>
<tr>
<td>0.133</td>
<td>510</td>
<td>5</td>
</tr>
<tr>
<td>0.133</td>
<td>605</td>
<td>6</td>
</tr>
</tbody>
</table>
Fig. 10. Ultimate tensile strength versus temperature determined at a strain-rate of 0.0093 min$^{-1}$. Arrows indicate the maximum and minimum temperatures at which serrations occur.
Fig. 11. Ultimate tensile strength versus temperature determined at a strain-rate of 0.0149 min⁻¹. Arrows indicate maximum and minimum temperatures at which serrations occur.
Fig. 12. Ultimate tensile strength versus temperature determined at a strain-rate of 0.133 min\(^{-1}\). Arrows indicate maximum and minimum temperatures at which serrations occur.
Several techniques are available for this calculation. Each of these is based on the assumption that the temperature and strain-rate of a particular peak are related by an equation of the form:

\[ \dot{\varepsilon} = Ae^{-Q/RT} \]  

(4)

where \( \dot{\varepsilon} \) is the strain-rate; \( A \), a constant; \( Q \), the activation energy for the process responsible for the peak; \( R \), the gas constant; and \( T \), the temperature in °K. From Equation 4 it can be seen that a plot of \( \log \dot{\varepsilon} \) versus \( 1/T \) should result in a straight line, the slope of which is \( \frac{-Q}{2.303R} \). Plots of this type were chosen for the determination of the activation energies in this investigation. The data from Table 5 have been plotted in this manner, and the results are shown in Fig. 13. Activation energies calculated from slopes drawn through points 1, 3, and 5 and points 2, 4, and 6 were each found to be approximately 12,000 cal mole\(^{-1}\). This value does not correspond to that for any known mechanism describing the existence of strain-aging peaks. If, however, the slopes are drawn between points 1, 3, and 6 and points 2, 4, and 5 activation energies of 7,400 and 22,400 cal mole\(^{-1}\) are obtained. The higher value is in good agreement with that noted by Weaver (14) and de Morton (15) for the activation energy for
Fig. 13. Plot of lot strain-rate versus $1/T$ for the determination of the activation energies associated with the strain-aging peaks
diffusion of nitrogen in chromium.

If this calculation is correct and the peaks are actually changing relative position with increasing strain-rate, Fig. 13 shows that only one peak should exist at a strain-rate of \(0.0585 \text{ min}^{-1}\) and a temperature of 465°C. The occurrence of this single peak has been verified experimentally as is shown in Fig. 14. In future discussions this peak will be referred to as peak 7.

On the basis of this activation energy and the "viscous drag" mechanism proposed by Nabarro (8), it can be concluded that peaks 2, 4, and 5 are apparently due to the diffusion of a nitrogen impurity cloud along with the moving dislocation in a manner similar to that responsible for the strain-aging peak caused by carbon and nitrogen in iron.

Fig. 10 also shows the dynamic strain-aging characteristics of a 140 ppm nitrogen alloy strained at \(0.0149 \text{ min}^{-1}\). It can be seen that this curve is again characterized by the occurrence of a double strain-aging peak. Because of the extremely low solubility of nitrogen in chromium, it is reasonable to assume that the additional interstitial in this alloy would be present completely as second phase chromium nitride. In this form it would not be expected to alter the
Fig. 14. Ultimate tensile strength versus temperature determined at a strain-rate of 0.0585 min$^{-1}$. Arrows indicate maximum and minimum temperatures at which serrations occur.
amount of nitrogen in free solution. Hence, if the 410°C peak in the low nitrogen material is actually a nitrogen diffusion peak governed only by the nitrogen in solution, it would not be expected to be altered by the further addition of nitrogen. If the above reasoning is accepted it then appears that increasing the amount of nitride precipitate present shifts the 300°C peak to 500°C.

These observations are in agreement with the results of Weaver (34) illustrated in Fig. 3. He has also observed the presence of a double strain-aging peak in chromium. While the impurity content and strain-rate values differ for the two investigations, both studies coincidentally find peaks at 300 and 400°C in the lowest nitrogen alloy tested. Weaver finds that increasing the nitrogen content from the original 0.0005 to 0.002% results in an increase in the peak temperatures to 400 and 620°C. Here again it is not unreasonable to assume that the increase in nitrogen content has shifted the 300°C peak to 620°C while leaving the diffusion controlled peak at 400°C unaltered.

If the above reasoning is correct it would appear that the activation energy associated with this nitride dependent peak would also be a function of the nitrogen concentration.
A mechanism is proposed, however, which suggests that while additional nitride precipitate does result in an increase in the actual peak temperature, the relative change in this temperature with varying strain-rate would not be altered and an identical activation energy would be obtained. Further discussion of this point will be deferred until after an outline of this model has been presented.

As is characteristic of a material influenced by the effects of dynamic strain-aging, the strain-rate sensitivity of chromium shows a broad minimum in the strain-aging region as is shown in Fig. 15. Because of the limited temperature range over which tests were conducted, it is not possible to state conclusively that this temperature dependence follows a form typical of strain-aging as illustrated in Fig. 2. It is assumed, however, that additional data at the temperature extremes would confirm a normal temperature variation outside the strain-aging region. It is interesting to note that, for the most part, this curve is independent of strain-rate and nitrogen concentration. Recovery from the minimum, however, does seem to occur at a slightly lower temperature in the higher nitrogen alloy. The strain-rate sensitivity was not observed to exhibit a negative value under any conditions,
Fig. 15. Strain-rate sensitivity versus temperature for several sets of testing conditions
which is in agreement with the observations of Pugh (30). However, Weaver (34) has noted a negative strain-rate sensitivity in the strain-aging region. The strain-rate sensitivity did become zero in several instances.

Discontinuous yielding was observed under all conditions of nitrogen concentration and strain-rate studied. The maximum and minimum temperatures at which serrations occurred are identified in Figs. 10-12, and 14, and these data are tabulated in Table 6 along with the approximate temperature at which the serrations are most intense.

Table 6. Summary of the temperature and strain-rate data for the occurrence of serrations

<table>
<thead>
<tr>
<th>Nitrogen content, ppm</th>
<th>Strain-rate min⁻¹</th>
<th>Temperature °C</th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Minimum</td>
<td>Maximum</td>
<td>Most intense</td>
<td></td>
</tr>
<tr>
<td>30</td>
<td>0.0093</td>
<td>225</td>
<td>500</td>
<td>300-325</td>
<td></td>
</tr>
<tr>
<td>30</td>
<td>0.0149</td>
<td>250</td>
<td>530</td>
<td>350-375</td>
<td></td>
</tr>
<tr>
<td>30</td>
<td>0.0585</td>
<td>300</td>
<td>600</td>
<td>460-500</td>
<td></td>
</tr>
<tr>
<td>30</td>
<td>0.133</td>
<td>475</td>
<td>650</td>
<td>600-625</td>
<td></td>
</tr>
<tr>
<td>140</td>
<td>0.0149</td>
<td>400</td>
<td>520</td>
<td>460-485</td>
<td></td>
</tr>
</tbody>
</table>

Fig. 16 illustrates the shape of the observed flow curves along with examples of these serrations for several series of tests.

While little quantitative information can be derived
Fig. 16. Typical examples of the flow curves obtained for several sets of testing conditions
from the characteristics of these serrations, it is possible as suggested by Boniszewski and Smith (77) to determine the activation energy associated with the process responsible for this effect. They point out that if, as had been suggested in Section II, these serrations are a result of repeated locking and unlocking of the moving dislocation, then the strain-rate and temperature at which they occur should be related by an equation similar to Equation 4. If then a temperature can be determined at each strain-rate for which the degree of discontinuous yielding is equivalent, an activation energy can be calculated through the slope of a log $\dot{\varepsilon}$ versus $1/T$ plot. Taking this equivalent temperature to be the maximum temperature at which serrations were still observed, the plot shown in Fig. 17 can be constructed and an activation energy of 24,700 cal mole$^{-1}$ is found for the mechanism occurring in chromium. Since this value is again in reasonable agreement with the activation energy for the diffusion of nitrogen in chromium, it seems reasonable to attribute the occurrence of these serrations to the repeated locking of the moving dislocation by its nitrogen atmosphere. It is interesting to note that while the serrations in the nitrogen alloy are considerably less intense than in the iodide
Fig. 17. Plot of log strain-rate versus 1/T for the determination of the activation energy associated with the occurrence of serrations
$Q = 24,700 \text{ CAL MOLE}^{-1}$
material and occur over a much narrower temperature range, they are observed to terminate at the same temperature as was noted at an equivalent strain-rate in the low nitrogen material. This similarity would be expected since the re-locking mechanism as proposed by Nabarro (8) would be dependent only on the amount of interstitial in solid solution and would not be altered by additional second phase particles.

The yield strength of chromium has been observed to show the same trends toward strain-aging maxima as were noted in the ultimate tensile strength. The magnitudes of these peaks, however, were only 15-20% of those observed in the ultimate tensile strength. As can be seen from Fig. 16 the occurrence of the yield point was found to be strongly affected by the nitrogen concentration. Increasing the nitrogen level from 30 to 140 ppm greatly diminished the occurrence of the yield point as it reduced the intensity of serrations. From these observations it would appear that the additional nitride precipitate present in the 140 ppm alloy has, in some manner, masked the drop in load which ordinarily would occur as the dislocation is pulled free of its atmosphere.

Reproducible ductility data on chromium was difficult to obtain because of the material's extreme sensitivity to sur-
face condition and axial alignment during testing. Under all conditions of strain-rate, nitrogen concentration, and temperature tested, the reduction in area was found to be greater than 95% and thus no strain-aging effects were observed. The uniform elongation, however, did show noticeable trends toward minima at the temperatures at which strain-aging peaks were observed in the ultimate tensile strength. While these trends were somewhat obscured by lack of precision caused by the above factors, data obtained at a strain-rate of 0.133 min$^{-1}$ show this phenomenon quite effectively. These results are shown in Fig. 18. These observed minima would be expected if an impurity atmosphere is hindering the motion of a moving dislocation according to the mechanism of Nabarro (8).

On the basis of the above observations, it appears that the strain-aging peak associated with the activation energy of 22,400 cal mole$^{-1}$ can safely be attributed to the diffusion of a nitrogen atmosphere along with the moving dislocation. The mechanism responsible for the second peak, however, is still unclear. Of the possible explanations available such as hydrogen diffusion, vacancy diffusion, and Snoek ordering, each can be discarded on the basis of the
Fig. 18. Example of the minimums in uniform elongation resulting from strain-aging. Strain rate: 0.133 min⁻¹
experimental evidence. The activation energy and strain-rate dependence observed for this peak would not be expected for either vacancy diffusion or Snoek ordering. While the value of 7,400 cal mole\(^{-1}\) is not unreasonable for the activation energy of hydrogen diffusion in chromium, a hydrogen peak would not be expected at these high temperatures. In addition none of the above processes present a reasonable explanation for the dependence of the peak temperature on the presence of additional nitride precipitate.

One possible explanation for the occurrence of these peaks, however, can be suggested on the basis of a recent proposal by Gibbs (78). He has postulated that another process exists, in addition to those proposed by Cottrell, through which interstitial atoms might interact with a dislocation. In his model Gibbs suggests that as a dislocation is bowed out from its original source, a lateral force is exerted on the impurity atoms bound to the dislocation, and this force can cause the impurity atoms to diffuse along the dislocation line. He has determined this lateral force \(F\) to be predicted by the equation:

\[
F \approx \sigma^2 \frac{b^3}{2\mu} (m^2 - n^2)
\]

where \(\sigma\) is the applied stress; \(b\), the Burgers vector of the
dislocation; \( \mu \), the shear modulus; and \( m \) and \( n \) the number of lattice spaces between impurity atoms on the dislocation. The manner in which this process operates is shown schematically in Fig. 19 and can be outlined in the following manner. As the original dislocation shown in Fig. 19a begins to move under the action of an applied stress, the impurity atoms move with it for a short distance. With the increasing length of the expanding dislocation a decrease in the linear density of solute atoms occurs, and these solute atoms begin to move laterally along the dislocation line. As straining is continued a segment of solute free dislocation such as CD in Fig. 19b appears, and the length of CD and similar segments increase until the largest loop reaches the critical length, \( \mu/\sigma \), required for generator operation (see Fig. 19c). Past this point the dislocation is no longer held up by the presence of impurity atoms, and generation continues in a normal fashion. The sweeping dislocation annihilates segments such as AC and DB before further diffusion can take place, and the interstitial atoms associated with these segments are released to solution. It can be seen that the diffusion time required for attainment of the critical configuration shown in Fig. 19c is the controlling factor deter-
Fig. 19. Schematic diagram of the Gibbs model for the interaction of interstitial atoms with dislocations
mining the operation of the dislocation source and, therefore, the strength of the material. Gibbs has shown that this "unpinning time" ($t$) follows an equation of the form:

$$t \propto \exp \frac{Q}{RT}.$$  

At the temperature of a strain-aging peak resulting from this process, this unpinning time should be proportional to $1/\dot{\varepsilon}$ and, therefore, the strain-rate dependence of the peak would be given by an equation of the form:

$$\dot{\varepsilon} \propto \exp - \frac{Q}{RT}.$$  

The activation energy associated with this process would be expected to be equal to that required for dislocation-pipe diffusion of the interacting impurity. Brittain and Bronisz (79) have shown the activation energy for pipe diffusion of carbon in iron to be in the order of 8,500 to 10,000 cal mole$^{-1}$ or approximately one half that required for the normal diffusion of the interstitial. The value of 7,400 cal mole$^{-1}$ observed for the second strain-aging peak seems to be of the correct order of magnitude for this process. Also, this peak exhibits the same exponential relationship between strain-rate and temperature derived from the Gibbs model. It appears, therefore, that the model proposed by Gibbs presents a possible explanation for the existence of this second
strain-aging peak. On the basis of the data available the exact interstitial responsible cannot be determined. It does appear, however, that while the value of 7,400 cal mole\(^{-1}\) is more nearly one-third that for the diffusion of nitrogen as determined previously, this interstitial could well be the one responsible for this process since nitrogen has been shown to influence other facets of the behavior of chromium so significantly.

The observed shift of the 300°C peak to 500°C with an increasing amount of nitride phase is not incompatible with this line of reasoning. If the internodal distance of each dislocation source is decreased, as would occur with the addition of precipitate, the rate of linear increase in the dislocation length is necessarily increased to maintain the same component of dislocation velocity in the direction of straining. This higher rate requires a shorter unpinning time for source operation and, hence, a more rapid diffusion of interstitial. To attain this higher diffusion rate an increased temperature is required, and thus the peak temperature increases.

While this model predicts the temperature of the resulting strain-aging peak to vary with nitrogen concentration,
the relative difference in peak temperatures with varying strain-rate for any given nitrogen concentration should remain constant. The activation energy for the process, therefore, is not dependent on the nitrogen level. If, however, the activation energy is calculated on the basis of peak temperatures for materials of different nitrogen concentrations, an erroneous value would result since this model would view a change in the amount of precipitate to result in a metallurgically different material. Admittedly, this model is quite speculative, and additional research is suggested to elucidate the exact nature of this second peak.

2. Static strain-aging effects

As was pointed out in Section II, a number of investigators have observed the phenomenon of static strain-aging to be occurring in chromium. In order to obtain a more complete characterization of this process as it occurs in this material, the static strain-aging behavior of chromium has been studied as a function of both aging time and aging temperature. In addition to the variation in mechanical properties occurring during aging, the change in resistivity ratio was also measured as a function of the above variables in an attempt to independently determine the metallurgical
changes occurring.

Fig. 20 shows the change in the yield stress, flow stress, and resistivity ratio occurring during strain-aging as a function of aging temperature at a constant aging time of one hour. The mechanical parameters are defined by the insert in this figure. No evidence of strain-aging is observed at aging temperatures below 170°C. At this temperature the resistivity ratio begins to increase presumably as solute atoms are segregated to dislocations. No change in mechanical behavior is noted, however, since the amount of segregation is apparently insufficient to cause appreciable dislocation locking. After aging for one hour at 200°C, the occurrence of a yield point and an increase in flow stress are observed simultaneously. The magnitude of these quantities then continues to increase for progressively higher temperatures until a maximum is reached in \( \frac{\Delta \sigma_y}{\sigma} \) and \( \frac{\Delta \sigma_f}{\sigma} \) at 350 and 400°C respectively. Aging at higher temperatures results in an over-aging effect, and both values decrease to those observed at 450°C. The change in resistivity ratio also reaches a maximum value at 350°C and, subsequently, decreases at higher aging temperatures.

A second series of interrupted tensile tests were carried
Fig. 20. Increase in yield stress, flow stress, and resistivity ratio versus aging temperature for a constant aging time of one hour. Insert defines symbols.
Aging Temperature vs. (R_{300}/R_{42}) UNAGED

\( \Delta \sigma / \sigma \)

\( \Delta \sigma_y / \sigma \)

\( \Delta \sigma_t / \sigma \)

Aging Temperature, °C
out at varying aging times and constant aging temperatures of 250, 350, and 450°C respectively. The return-of-yield point and flow stress data for this series are shown in Fig. 21, while the change in resistivity ratio on aging is presented in Fig. 22. In addition to these properties, the yield point elongation and change in work-hardening coefficient were calculated for this set of tests, and these results are shown in Fig. 23. It can be seen from these data that increasing the aging temperature results in a change in the form of the time dependency of the static strain-aging characteristics of chromium. At 250°C the \( \frac{\Delta \sigma_y}{\sigma} \) and \( \frac{\Delta \sigma_f}{\sigma} \) begin to increase simultaneously after aging for 20 min. Both of these quantities show a maximum after 30 min and, subsequently, decrease on continued aging with \( \frac{\Delta \sigma_f}{\sigma} \) becoming zero after 60 min aging time while \( \frac{\Delta \sigma_y}{\sigma} \) reaches a constant value of 0.04 at this point. At 350°C no strain-aging effects were observed after aging for 5 min while maximum values of both \( \frac{\Delta \sigma_y}{\sigma} \) and \( \frac{\Delta \sigma_f}{\sigma} \) are noted on aging for 10 min. Longer aging times result in a gradual decrease in both quantities as shown.

Reliable data could not be obtained for aging times of less than 5 min by this technique, and thus the exact nature
Fig. 21. Increase in yield stress and flow stress versus aging time at constant aging temperatures as noted.
Fig. 22. Change in resistivity ratio versus aging time at constant aging temperatures as noted
Fig. 23. Yield point elongation and change in work-hardening coefficient versus aging time at constant aging temperatures as noted.
The graph shows the changes in yield point elongation and change in work hardening coefficient over aging time at three different temperatures: 250°C, 350°C, and 450°C. The x-axis represents aging time in minutes, and the y-axis represents percent yield point elongation and change in work hardening coefficient.
of the initial strain-aging characteristics at $450^\circ C$ could not be determined. It appears, however, that $\left( \frac{\Delta \sigma_y}{\sigma_f} \right)$ and $\left( \frac{\Delta \sigma_f}{\sigma_f} \right)$ again show maximum values as aging begins and a subsequent decrease at longer aging times.

The change in resistivity ratio ($\Delta R$), yield point elongation ($\Delta \eta$), and change in strain-hardening coefficient ($\Delta n$) show similar changes in their time dependency with increasing aging temperature. At $250^\circ C$, $\Delta R$ and $\Delta n$ show a maximum and minimum value respectively at an aging time of 30 min while the $\Delta \eta$ shows a small maximum at 20 min before gradually increasing at longer times. At $350^\circ C$ the $\Delta \eta$ and $\Delta n$ versus temperature curves exhibit a form similar to those at $250^\circ C$ with the minimum in $\Delta n$ occurring at 20 min in this case. The resistivity ratio, however, shows a more gradual increase than that observed at $250^\circ C$ with the maximum occurring at 90 min aging time. A sharp change in the form of these curves is noted on increasing the aging temperature to $450^\circ C$. The $\Delta R$ and $\Delta n$ curves show sharp increases and the $\Delta \eta$ curve decreasing abruptly during the first 20 min of aging while becoming nearly constant at longer times.

As can be seen from the above data, aging effects begin to appear after relatively short periods of time at these
temperatures. Because of the time necessary for the sample to reach the temperature of an external aging bath and difficulties in reproducing the original alignment of the specimen on returning the sample to the tensile equipment, accurate measurement of the small effects occurring at these short aging times was not possible. In addition, the above data affords no way to calculate an activation energy for the process responsible for the return-of-yield point in chromium. In order to study these initial effects, a series of tests were carried out at various temperatures during which the samples were repeatedly strained just beyond the yield point, unloaded, and aged at test temperature. During the aging step the sample was held under a slight load to insure a consistent sample alignment. If the Cottrell-Bilby equation (Equation 1) describes the return-of-yield point process as it occurs in chromium, and if it is assumed, after Bolling (80), that \( \frac{\Delta \sigma_y}{\dot{\gamma}} \) is proportional to the amount of solute segregated to the dislocation, then a plot of \( \log \left( \frac{\Delta \sigma_y}{\dot{\gamma}} \right) \) versus \( \log t \) should result in a straight line. The results of the above series of tests are plotted in this manner in Fig. 24. The solid symbols in this figure represent aging times for which an observable increase in flow
Fig. 24. Log \( \left( \frac{\Delta \sigma}{\sigma} \right) \) versus log \( t \) for constant aging temperature as noted.
stress is noted along with the return-of-yield point. Since Fig. 24 shows a straight line to result from this treatment of these data, it then seems that the Cottrell mechanism for the return-of-yield point is responsible for the effects noted in chromium.

Since the observed return-of-yield point is a diffusion controlled process, it would be expected that this property should follow an equation of the form:

\[ \frac{1}{t} \propto e^{-Q/RT} \]

If, then, a time \( t \) can be determined which represents equivalent segregation of interstitials at each aging temperature, a plot of \( \log \frac{1}{t} \) versus \( 1/T \) should yield a straight line, the slope of which is equal to \( \frac{-Q}{2.303R} \). Assuming that equal values of \( \frac{\Delta \sigma_Y}{\sigma} \) represent this equivalent aging, the times necessary to attain this degree of segregation can be determined from Fig. 24, and the plots shown in Fig. 25 can be drawn. It can be seen from this figure, however, that these data do not give the predicted straight line, and it appears that equal values of \( \frac{\Delta \sigma_Y}{\sigma} \) do not represent equivalent degrees of segregation as supposed. Considering the data given in Fig. 24, it is not unreasonable to assume that the contribution of strain-age hardening to \( \frac{\Delta \sigma_Y}{\sigma} \) invalidates
Fig. 25. Log 1/t versus 1/T for several values of \((\Delta \sigma_y)\). The slopes used to calculate the activation energy for the process responsible for the return-of-yield point are illustrated.
this assumption, and a change in the slope of the log $t$ versus $1/T$ results in the region where this precipitation is occurring. At lower aging temperatures, however, little strain-age hardening is observed, and in these cases the above assumption should still be valid. If, then, the slope used for the calculation of the activation energy is based on points determined in these regions, a reasonable value for this energy can be calculated. Fig. 25 shows the slopes determined in this manner and from these, an average activation energy of 18,700 cal mole$^{-1}$ is found. While this value is considerably lower than those previously attributed to nitrogen diffusion processes, it is still within the range of activation energies reported by Weaver (14) for the diffusion of nitrogen in chromium. A value determined in this manner might be anomalously low according to an argument by Weaver. He points out that the diffusion distances, in this case one-half the distance between dislocations, should be constant for the various aging temperatures in order to obtain reasonable diffusion data. Since these samples were strained at different temperatures, it is not unreasonable to assume that the dislocation spacings for each temperature are not equal and that this results in a slight uncertainty.
in the calculated activation energy. Also, the apparent sensitivity of this calculation to the value of \( \frac{\Delta \sigma}{\sigma} \) chosen to represent equivalent segregation can result in additional error. On the basis of this value then, it appears that the return-of-yield point observed in chromium is a result of the relocking of freed dislocation by the same nitrogen atmosphere responsible for the dynamic strain-aging characteristic previously described.

Because of the combination of processes found to be operating during the static strain-aging of chromium, it is difficult to interpret all of the observed phenomena on the basis of known mechanisms. Several observations can be made, however, regarding the effects of these mechanisms on the behavior of chromium.

One significant result of this phase of the investigation is the determination of an activation energy near that for the diffusion of nitrogen in chromium. The linear relationship between \( \log \left( \frac{\Delta \sigma}{\sigma} \right) \) and \( \log t \) shown in Fig. 24 suggests that this interstitial is being segregated to the dislocations by a mechanism of the type proposed by Cottrell. This conclusion is supported by the initial increase in the resistivity ratio noted on aging which is indicative of a
decrease in the number of solute atoms existing in free solution, presumably as a result of their segregation to dislocations.

From the data presented in Fig. 20 and 21 it appears that a simultaneous return-of-yield point and increase in flow stress is occurring. Data shown in Fig. 24, however, indicate that at lower aging temperatures at least the yield point return is observed prior to the occurrence of strain-age hardening. The observation of these strain-age hardening effects is in agreement with the results of Metcalfe et al. (32) and Weaver (36), and these effects appear to result from a precipitation mechanism similar to that proposed by Hundy (18) for the increase in flow stress in iron. As these data show, increasing the aging temperature results in a more rapid formation of the precipitates on the dislocations. This simultaneous precipitation is not unreasonable considering Weaver's estimate that a nitrogen atom is bonded to a dislocation with an interaction energy of 0.45 ev while its interaction energy with a precipitate particle is 1.0 ev. It would thus be expected that precipitation would begin as soon as a sufficient number of nitrogen atoms have segregated to the dislocation to cause the nucleation of a precipitate.
As this precipitation occurs, the interstitial atoms exist in a wide variety of distribution states ranging from dislocation atmospheres and coherent precipitates to an incoherent nitride phase. The interpretation of these phenomenon is further complicated by the apparent reversal of the relative dislocation atmosphere-precipitate stability observed in other body-centered-cubic metals. The superposition of the contributions of these various states of aggregation to the observed strain-aging effects results in the complicated behavior described above. A greater knowledge of the precipitation process in general and the dislocation initiated precipitation process in particular is necessary before the static strain-aging behavior of chromium can be completely understood.

B. The Brittle-Ductile Transition

Previous investigators have left little doubt that nitrogen has a definite influence on the ductility transition in chromium. The exact nature of this nitrogen effect, however, appears to be dependent not only on the concentration of the interstitial but also on its distribution in the lattice. The prime concern of this phase of the investigation is to study the joint effect of these variables experimentally and
to attempt to correlate these observations with existing theories.

Because of the difficulties encountered in controlling the grain size of the polycrystalline chromium with varying nitrogen concentration and the sensitivity of the transition temperature to the grain size (66), most tests were carried out on single crystals. In two cases, however, data were obtained on the transition temperature of polycrystalline chromium which verified the observations of other investigators. These data are presented in Table 7 along with comparable data from other sources.

Plots of transition temperature versus nitrogen content for the single crystal specimens are shown in Fig. 26 for both the furnace-cooled and quenched conditions. It will be noted that nitrogen has a greater effect on the transition temperature in the slow-cooled condition than in the quenched state.

It thus appears from a comparison of Fig. 26 and Table 7 that the effects noted in the polycrystalline specimens are reversed in the single crystals. Quenching was found to raise the transition temperature of the polycrystal quite markedly but had little or no effect on the transition tem-
Table 7. The effect of nitrogen on the transition temperature of polycrystalline chromium

<table>
<thead>
<tr>
<th>Condition</th>
<th>Nitrogen content</th>
<th>Grain size</th>
<th>Transition temperature °C</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Furnace-cooled</td>
<td>50 ppm</td>
<td>40/\text{mm}^2</td>
<td>40° 5</td>
<td>Present work</td>
</tr>
<tr>
<td>Quenched*</td>
<td>50 ppm</td>
<td>40/\text{mm}^2</td>
<td>165° 10</td>
<td></td>
</tr>
<tr>
<td>Slow cooled</td>
<td>50 ppm</td>
<td>20/\text{mm}^2</td>
<td>20° 5</td>
<td></td>
</tr>
<tr>
<td>Slow cooled</td>
<td>125 ppm</td>
<td>22/\text{mm}^2</td>
<td>10° 5</td>
<td></td>
</tr>
<tr>
<td>Slow cooled</td>
<td>125 ppm</td>
<td>22/\text{mm}^2</td>
<td>135° 5</td>
<td></td>
</tr>
<tr>
<td>Slow cooled</td>
<td>75 ppm**</td>
<td>-</td>
<td>300°</td>
<td>61</td>
</tr>
<tr>
<td>Slow cooled</td>
<td>75 ppm**</td>
<td>-</td>
<td>390°</td>
<td></td>
</tr>
<tr>
<td>Slow cooled</td>
<td>175 ppm**</td>
<td>-</td>
<td>290°</td>
<td></td>
</tr>
<tr>
<td>Slow cooled</td>
<td>175 ppm**</td>
<td>-</td>
<td>490°</td>
<td></td>
</tr>
<tr>
<td>Slow cooled</td>
<td>20 ppm N</td>
<td>-</td>
<td>380°</td>
<td>62</td>
</tr>
<tr>
<td>Slow cooled</td>
<td>300 ppm N</td>
<td>-</td>
<td>350°</td>
<td></td>
</tr>
</tbody>
</table>

*This specimen was water quenched from a salt bath at 900°C.

**Total C, N, and O content with nitrogen is the principal interstitial.
Fig. 26. Nitrogen concentration vs transition temperature for chromium single crystals
perature of the single crystals at low nitrogen concentrations while actually decreasing the transition at higher nitrogen levels. In the furnace-cooled condition an increase in the nitrogen content raises the transition temperature of the single crystals rather appreciably but has no observable effect on the polycrystalline specimens.

From the above observations it was concluded that the effect of nitrogen on the ductility of chromium is dependent to a large degree on the presence of grain boundaries. To investigate this dependency, series of single and polycrystalline specimens were charged to 225 and 125 ppm N respectively. These samples were then quenched and aged at 200°C for times ranging from 10 min to 19 hours. Transition temperatures for this series were determined, and the results are shown as a function of aging time for the single and polycrystalline specimens in Figs. 27 and 28. The polycrystalline specimens exhibit a sharp decrease in transition temperature during the first 40 min of aging while the single crystals show no change over the same period of time. Continued aging results in an increase in the brittle-ductile transition temperature for both types of specimens.

Electron micrographs of samples after various aging
Fig. 27. Transition temperatures vs aging time at 200°C for single crystal chromium containing 225 ppm nitrogen
Fig. 28. Transition temperature vs aging time at 200°C for polycrystalline chromium containing 125 ppm nitrogen
times show a gradual increase in and coarsening of the precipitate particles during the aging treatment. Fig. 29 shows the changes in appearance of the precipitate during aging. In the quenched material a small amount of a very fine precipitate is present, while aging for 40 min produces considerably more precipitate but of approximately the same size. Heating for longer periods results in a coarsening of the particles as is shown in Fig. 29c which shows the particles after aging for 19 hours. Fig. 30 shows a typical example of the precipitate produced on furnace-cooling. From a comparison of Fig. 29c and 30 it will be noted that furnace-cooling produces much larger nitride particles than are obtained even after aging for 19 hours at 200°C.

In agreement with the observations of Hook et al. (66) and McNeil and Limb (69) a fractographic study of the polycrystalline specimens indicates that cracks nucleate at the grain boundaries and proceed transgranularly to cause fracture (see Fig. 31). The mode of crack initiation appears to change with aging time in the single crystals. For aging times up to 40 min the fracture nucleates from a single source usually on the surface (see Fig. 32) while after longer times the fracture proceeds from a series of secondary
Fig. 29. Electron micrographs of chromium single crystals containing 225 ppm nitrogen: (a) as quenched, (b) aged 40 min, (c) aged 1140 min. Carbon replica, X6000
Fig. 30. Typical nitride precipitate in a furnace cooled chromium single crystal containing approximately 1000 ppm nitrogen. X250
Fig. 31. Fractograph of typical polycrystalline fracture initiation site. X200
Fig. 32. Fractograph of typical single crystal fracture for specimens aged less than 40 min. X20

Fig. 33. Fractograph of typical single crystal fracture for specimens aged longer than 40 min. X20
sources within the specimen, leading to an irregular frac-
ture surface (Fig. 33). A similar difference was observed
between quenched and furnace-cooled samples.

In studying the brittle-ductile transition in chromium
one may consider the problem of brittle fracture in two
stages, crack nucleation and crack propagation. As has been
noted previously, both of these mechanisms have been postu-
lated to be the rate controlling step in the occurrence of
brittle fracture in chromium. From the data obtained during
this investigation, it appears that both of these processes
are capable of operating in this capacity, and the respon-
sible mechanism in any particular case is dependent on the
condition of the material.

Considering the data presented in Figs. 27 and 28, a
dercrease is noted in the transition temperature of poly-
crystalline chromium during the first hour of aging at 200°C,
but no change occurs in the single crystals to this point.
Comparing this with Weaver's observations on the precipita-
tion of the nitride in chromium (see Fig. 1), this aging time
corresponds to the period in which there is a sharp decrease
in the resistivity. Since Weaver attributes this decrease
in resistivity to a decrease in the nitrogen in solid solu-
tion due to precipitation of a nitride phase, it may be assumed that this same phenomenon is responsible for the initial decrease in the polycrystalline transition temperature.

One possible explanation of the above behavior can be visualized if a crack is considered to be nucleated by a pile-up of dislocations at grain boundaries such as has been suggested by Zener (73). Since no change in the grain structure occurs during aging at such low temperatures, grain boundaries should be constant sources for crack nucleation in the polycrystals, and crack propagation should then be the controlling factor in brittle fracture, barring the introduction of additional crack initiation sites. According to the argument presented by Weaver and Gross (75) and outlined in Section II, the rate of this propagation is governed by the nature of dislocation motion near the tip of the crack. If dislocation flow across the crack tip is easily accomplished, the rate of crack propagation is slowed. If, however, the flow of dislocations is inhibited in some manner, crack propagation takes place more readily, and the tendency toward brittle failure is increased. It can be assumed then that the decrease in transition temperature,
resulting on initial aging of the polycrystalline chromium, results from an increase in the ease of plastic deformation near the crack tip. On the basis of Weaver's observation on the precipitation of nitrogen from solid solution during aging, it seems that the observed drop in transition temperature with short aging times for multigrained chromium may be attributed to a decrease in Cottrell locking resulting from clustering or precipitation of interstitial impurities from quenched solution.

While this seems a reasonable explanation for the observed decrease, recent speculation regarding action of precipitate particles as dislocation sources makes another possible mechanism available. As shown by the electron micrographs in Fig. 29, a large increase in the number of precipitate particles takes place during the first 40 min of aging. If these particles are assumed to be acting as dislocation sources, it seems reasonable to speculate that increasing the number of these sources would increase the likelihood of plastic flow and in turn decrease the tendency toward brittle failure.

Crack nucleation, however, would appear to control the fracture process in the single crystals since no grain
boundaries or second phase particles of significant size are present to contribute readily available crack embryo. Hence, no change in the transition temperature occurs upon aging until the nitride particles reach a sufficient size and concentration to serve as barriers against which dislocation pile-up can occur. After aging for one to two hours the precipitate appears to reach this critical size dimension, and the transition temperatures of both the single and polycrystalline materials increase rather sharply with increasing aggregate size. This increase is believed to be the result of two effects both of which can be attributed to the presence of these dislocation pile-ups. First, the dislocation pile-up can coalesce and nucleate cracks as described above. Secondly, the occurrence of these dislocation pile-ups reduce the motion of dislocations near the crack tip and, therefore, increase the speed of crack propagation.

If aging were carried out at higher temperatures or for prolonged periods of time, the transition temperature of both the single and polycrystalline specimens would be expected to approach their respective furnace-cooled values.

Fractographic evidence presented in Figs. 32 and 33 supports the conclusion that a change in the fracture
mechanism occurs during the aging process in the single crystals. For aging times up to 40 min fracture initiates at one point and proceeds across the specimen from a single source. After aging for longer periods of time several secondary crack initiation sites appear, and the fracture surface is quite irregular as would be expected if the multiple sources and stress concentrations caused by the precipitates were present.

This explanation is consistent with the data showing the effect of nitrogen concentration on the single crystal presented in Fig. 26. The observed increase in transition temperature with nitrogen concentration would be expected from the increased amount of nitride phase present which should enhance the ease of crack nucleation and also inhibit plastic flow in the vicinity of the crack tip. Upon quenching, the nitrogen is retained in solution and, in the absence of either precipitate particles or grain boundaries to nucleate a crack, the transition temperature is appreciably lower and relatively independent of nitrogen content.

In the polycrystalline specimens, on the other hand, quenching raises the transition temperature rather markedly from that of the furnace-cooled specimens for all nitrogen
concentration and grain sizes. If cracks are considered to be readily initiated at grain boundaries, crack propagation should thus control the transition temperature. The quenching of nitrogen into solid solution results in an overall reduction in the ductility of the matrix, thus resulting in a higher transition temperature due to a greater ease of crack propagation across the grain.

It is interesting to note that a similarity exists between the furnace-cooled and the quenched and aged specimens in that both show an increase in transition temperature with an increasing precipitate array. Fractographic studies also show a similarity in the fracture mechanism between these specimens, indicating that both are "multiple source", precipitate-initiated fractures.
VI. SUMMARY

While the previous section illustrates in some detail the experimental results obtained during the course of this investigation and describes the theoretical conclusions which have been made where possible, it seems appropriate to summarize the major observations of this investigation in a concise form.

All of the characteristics suggested as being typical of a material which exhibits the effects of dynamic strain-aging have been observed in chromium. The ultimate tensile strength versus temperature curves are characterized by the existence of a double strain-aging peak, and from an investigation of the strain-rate dependence of these peaks, it has been possible to determine that both are controlled by diffusion processes with activation energies of 22,400 and 7,400 cal mole$^{-1}$ respectively. The value of 22,400 cal mole$^{-1}$ is in reasonable agreement with that determined for the diffusion of nitrogen in chromium, and thus it appears that the existence of this peak is almost certainly a result of the diffusion of a nitrogen impurity atmosphere along with the moving dislocation. The mechanism responsible for the second peak is still unclear; however a possible explanation has
been outlined on the basis of the dislocation-pipe diffusion model proposed by Gibbs.

Serrations were observed in the strain-aging region under all conditions of strain-rate and nitrogen concentration studied, and an activation energy of 24,700 cal mole\(^{-1}\) has been determined for this phenomenon. This is again in fair agreement with the value associated with the diffusion of nitrogen in chromium, and it appears that unlocking and re-locking of the moving dislocation by a nitrogen impurity cloud similar to that causing the maximum in the ultimate tensile strength is responsible for these discontinuities.

Minimums in the strain-rate sensitivity and uniform elongation were also observed in the strain-aging temperature range as would be expected if a nitrogen atmosphere is inhibiting the motion of the dislocation.

The static strain-aging behavior of chromium is characterized by the nearly simultaneous occurrence of the return-of-yield point and strain-age hardening at higher aging temperatures. The existence of this precipitate on the dislocation line prevents the determination of the activation energy associated with the yield point return since the magnitude of the yield point cannot be taken as representing the amount
of interstitial segregation which has occurred. If, however, the calculation of the activation energy is based on aging conditions which do not result in observable strain-age hardening, a value of 18,700 cal mole\(^{-1}\) is obtained. While this value is somewhat lower than those previously attributed to the diffusion of nitrogen, it is again within the range of the energy required for the diffusion of nitrogen in chromium and is further evidence of the importance of nitrogen in determining the mechanical behavior of chromium. The nature of the strain-age hardening process in chromium has been shown to be quite complex, and a complete description of the process must be deferred until a more complete understanding of the precipitation processes occurring in chromium has been obtained.

The effect of nitrogen on the brittle-ductile transition in chromium has been shown to be dependent on both the presence of grain boundaries and the distribution of the interstitial. Increasing the nitrogen concentration in furnace-cooled polycrystalline chromium resulted in no change in the transition temperature while a significant increase was observed in the quenched material. These observations are reversed in the single crystals with nitrogen showing little
or no influence on the transition temperature in the quenched condition while a gradual increase is noted with increasing nitrogen content after furnace-cooling.

Continuously varying the nitrogen distribution in polycrystalline chromium through aging of quenched specimens results in an initial decrease in the transition temperature up to 40 min aging time followed by a sharp increase for longer times. In the single crystals no change in the transition temperature is observed up to 40 min while a sharp increase is again noted at longer times.

A model has been proposed relating these observations to the distribution of nitrogen and the presence of grain boundaries in the material. It is suggested that crack propagation is the controlling factor in determining the brittle fracture of polycrystalline chromium, and any mechanism which increases the ease of plastic flow in the material such as a decrease in the degree of Cottrell locking or the introduction of additional dislocation sources would lessen the probability of crack propagation and, therefore, decrease the transition temperature. In the single crystal, however, crack nucleation is the controlling factor, and no change occurs in the transition temperature until the ease with which this process
occurs is altered. In both single and polycrystalline chromium, precipitate particles of a critical size can act as sites for dislocation pile-up and thus serve as sources of crack nucleation as well as increase the ease of crack propagation through reducing the amount of dislocation motion occurring.

In summary then it has been shown that the presence of nitrogen greatly influences many phases of the mechanical behavior of chromium. While a mechanistic interpretation of the observed phenomenon has been proposed, the basic knowledge available does not permit the presentation of a complete explanation for all phases of the interaction of nitrogen with chromium.
VII. BIBLIOGRAPHY


VIII. ACKNOWLEDGEMENTS

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