The influence of precipitates on the brittle-ductile transition of chromium

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THE INFLUENCE OF PRECIPITATES ON THE BRITTLE-DUCTILE TRANSITION OF CHROMIUM

by

Robert Clark Tucker, Jr.

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INTRODUCTION

Progress in the technologies of aircraft engines, missiles, space vehicles, and nuclear power demands materials capable of maintaining high strength at ever increasing temperatures and often under very corrosive conditions. The refractory metals have received a considerable amount of attention in the search to satisfy these requirements.

Chromium melts at a lower temperature than any of the other refractory metals, but its melting point is nevertheless about 400°C higher than either nickel or cobalt, the base metals for most of the superalloys in common use. In addition it has relatively good oxidation resistance, better than any of the other refractory metals. Its low density, high modulus of elasticity, and abundance are all attributes which favor its use. The most important limiting factor in the utilization of chromium is its lack of ductility at room temperature. Since its brittle-ductile transition temperature occurs at about 300°C in commercial chromium, many problems arise in fabrication and service.

Interstitial impurities have been shown to be a primary cause of brittleness, not only in chromium, but in all the Group VI A metals. It is generally thought that the high transition temperature of the Group VI A metals compared to the Group V A is due to the much lower interstitial solubility limits in the Group VI A metals. Numerous studies have shown
that, in the case of chromium, nitrogen is the interstitial that has the greatest detrimental effect on the ductility. However, since the solubility of nitrogen is very low, much of the nitrogen present in the metal is probably in the form of a nitride. Thus the observations that the effect of nitrogen on the ductility is a function of the metal's thermal-mechanical history may reflect differences in the form in which nitrogen is present in the metal.

The role second phase particles play in the brittle-ductile transition of chromium is highly complex. For example, consider the frequently used equation for determining the transition:

\[(\sigma_0 d^{\frac{1}{2}} + k_y) k_y = \beta \omega \gamma\]

where \(\sigma_0\) is the internal frictional stress from the yield stress equation \(\sigma = \sigma_0 + k_y d^{-\frac{1}{2}}\), \(k_y\) is a measure of the stress required to propagate slip through a grain boundary, \(d\) is the grain diameter, \(\beta\) is a geometrical constant, \(\mu\) is the shear modulus, and \(\gamma\) is the surface energy term which includes plastic work. If the left-hand side of the equation is greater than the right, brittle behavior is observed; when the reverse is true, ductile behavior is observed. Second phase particles may have an effect on any of the variables.

The magnitude of the effect of a second phase particle on \(\gamma\) is dependent on whether or not the fracture is intergranular with the particle in the grain boundary or transgranular with the particle in the body of the grain. The
effect of a second phase on the yield stress is dependent on the average spacing between particles, their size, and coherency. The detrimental consequences of second phase particles may, however, be offset in one of two ways. If the second phase is the result of a compound formation involving the interstitial impurities, the removal of solutes from the lattice may produce a greater beneficial effect by lowering the yield stress than the detrimental effects of the resulting second phase. Alternatively, the second phase particles may serve as sources for dislocations and thereby lower the yield stress and the transition temperature.

Before the fabrication and service problems of chromium associated with its high brittle-ductile transition temperature can be alleviated it will be necessary to have a better understanding of the effects of interstitial impurities. The purpose of the present study is to contribute to this understanding by determining the effects of varying distributions of interstitial and precipitated nitrogen on the transition temperature. This will be accomplished by using a bend test to establish the transition temperature of a series of chromium-nitrogen alloys in the as-quenched condition and after a variety of aging treatments. The results will be correlated with resistance ratio, hardness, and yield strength data and interpreted in terms of the microstructural changes caused by the aging treatments.
LITERATURE REVIEW

The refractory metals, particularly Group VI A, have many properties in common and consequently much of the literature of one is of importance in the study of another. However, a comprehensive review of the brittle-ductile transition in refractory metals has recently been made by Schwartzberg et al. (1) so it will only be necessary to consider here the pertinent literature regarding chromium.

Edwards et al. (2) have thoroughly reviewed the work on chromium through 1958. Most of the research covered in their survey was performed on chromium prepared electrolytically or chemically reduced. These techniques were not capable of producing as pure a metal as the iodide process now used. Because of the high impurity content of the metal and the variety of testing methods used by the various investigators, interpretation of these early efforts is difficult. One of the salient facts discovered in the early work was that interstitials have an important influence on the brittle-ductile transition temperature of chromium. Increasing nitrogen concentrations were found to increase the transition temperature, most seriously in the recrystallized state. Carbon was found to have a similar effect, while oxygen and sulfur had only a slight effect on the transition temperature.

Although the purpose of this investigation is to more fully understand the effects of nitrogen on the transition
temperature, a brief summary of the other variables affecting the transition would seem to be pertinent as well.

Studies of Mechanical Properties

The advent of hydrogen purified electrolytic chromium and chromium produced by the iodide process have made possible more definitive studies of the various parameters affecting the brittle-ductile transition temperature. These investigations have included the properties of both high purity chromium and chromium to which deliberate additions of interstitial elements have been made. Metallic additions have also been studied, of course, but they are not of primary concern here. The brittle-ductile transition of chromium and its associated mechanical characteristics are controlled by the following factors: purity of the metal (only interstitials will be discussed here), thermal-mechanical history, grain size, surface condition, type of test, and strain rate. Before delving into some of these specific parameters it might be well to review some recent findings regarding the yield behavior of chromium.

Yield behavior

The plastic deformation of recrystallized chromium was investigated in compression by Marcinkowski and Lipsitt (3) from -195 to 400°C. Strain aging and strain age hardening were observed from 150 to 400°C. Others (4,5,6,7,8) have reported similar behavior for tensile studies and have also
found that the transition temperature in tension occurs in
the strain aging region. According to Marcinkowski and
Lipsitt (3) plastic deformation occurs by slip from -150 to
150°C with typical upper and lower yield points being exhibited except in the range -80 to 100°C. Within this range two successive upper yield points occur which were attributed to the penetration of subboundaries followed by the penetration of high angle grain boundaries by slip bands. The flow stress-grain size relationship $\sigma = \sigma_o + kd^{-1/2}$ is obeyed for the upper and lower yield points and for flow stress at 3% strain. The parameter $k$ is independent of temperature and strain rate and has the same value for all three flow stresses. It is associated with the stress necessary to drive dislocations into a grain boundary and then out into the next grain. Both temperature and strain rate have an effect on $\sigma_o$ which represents the shear stress necessary to overcome lattice friction.

The yield stress in compression increases almost linearly with a decrease in temperature from -10 to -150°C (3). Comparison with the data of others (4,7) shows that the fracture stress in tension also increases linearly with a decrease in temperature in a manner similar to the yield stress in compression.

Below -150°C Marcinkowski and Lipsitt (3) found that deformation was primarily by twinning. Since twinning was not observed in the present study it is felt unnecessary to
Cairns and Grant (9) and Gilbert et al. (10) indicate that increasing the rate of cooling after recrystallization increases the yield stress. Cairns and Grant (9) also found that a rapid rate of quenching was necessary for changes in interstitial content to have a significant influence on the yield stress.

**Brittle-ductile transition of unalloyed chromium**

The brittle-ductile transition temperature of high purity chromium has been investigated by a variety of tests within the last few years. It was generally found that this material exhibits a much lower transition temperature in the wrought than in the recrystallized condition. Furthermore a slow cooling rate after recrystallization produces greater ductility than quenching. A summary of recent work is presented in Table 1.

In the discussion which follows only changes in transition temperature due to a specific variable will be mentioned because differences in the type of test, grain size and impurity content make absolute comparisons questionable. This should also be borne in mind when considering Table 1.

**Effect of prestraining on the transition temperature**

The lower transition temperature of wrought compared to recrystallized chromium has led to investigations of the effect of prestraining on the transition temperature of the
Table 1. Results of recent brittle-ductile transition studies

<table>
<thead>
<tr>
<th>Reference</th>
<th>Analysis, ppm</th>
<th>Type of test</th>
<th>Condition of metal</th>
<th>Brittle-ductile transition temperature, °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>11</td>
<td>10 20 40</td>
<td>tensile</td>
<td>wrought</td>
<td>- 10</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>slow-cooled</td>
<td>300</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>oil-quenched</td>
<td>390</td>
</tr>
<tr>
<td>9</td>
<td>3 25 3</td>
<td>tensile</td>
<td>slow-cooled</td>
<td>135</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>hot oil-quenched</td>
<td>250</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>water-quenched</td>
<td>250</td>
</tr>
<tr>
<td>12</td>
<td>10 -- --</td>
<td>bend</td>
<td>slow-cooled</td>
<td>- 70</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>rapidly cooled</td>
<td>- 20</td>
</tr>
<tr>
<td>13</td>
<td>10 100 --</td>
<td>bend</td>
<td>wrought</td>
<td>- 30</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>slow-cooled</td>
<td>250</td>
</tr>
<tr>
<td>14</td>
<td>25 40 50</td>
<td>bend</td>
<td>slow-cooled*</td>
<td>- 90</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>oil-quenched*</td>
<td>- 70</td>
</tr>
<tr>
<td>15</td>
<td>2 20 15</td>
<td>notched</td>
<td>wrought</td>
<td>240</td>
</tr>
<tr>
<td></td>
<td></td>
<td>impact</td>
<td>slow-cooled</td>
<td>380</td>
</tr>
</tbody>
</table>

*Single crystals.
recrystallized material. Hook and Adair (5), Gilbert et al. (6) and Wain et al. (13) reported an increase in ductility with prestrain for slow-cooled, high purity material. These findings are in accord with earlier work on less pure material. It was also found that the amount of prestrain is not critical (6), and that the decrease in transition temperature is significantly diminished only after complete recrystallization (13), even though an upper yield point returns on aging at intermediate temperatures. Bullen et al. (16) found that pressurization before testing produces results similar to prestraining, in spite of the fact that no evidence of plastic strain could be found after this treatment. In contrast, Cairns and Grant (9) reported no effect due to prestraining on high purity chromium after quenching in air or water, but similar prestraining of oil-quenched material containing 180 ppm oxygen lowers the transition temperature 440°C.

**Effect of strain rate on the transition temperature**

The effect of strain rate on the transition temperature reported in the earlier literature has been substantiated in recent work (9,16,13), i.e. changes in strain rate have little effect at low rates regardless of interstitial content and high rates produce only moderate increases. Wood et al. (17) have described an intermediate state in the brittle-ductile transition found in static torsion testing and in tensile testing if the load is applied very slowly over a period of two or three days. This "sub-ductile" state is characterized
by creep in which the total strain is a function of the extent of creep allowed at each load, by constant fracture load, by mechanical hysteresis with up to 19% reversible plastic strain and by cyclic strain softening which is a function of the rate of cycling.

**Effect of grain size on the transition temperature**

The effect of grain size on the brittle-ductile transition temperature is somewhat open to debate. An anomalous behavior of increasing grain size causing a decrease in the transition temperature has been reported by several investigators (6,8,10). Hook and Adair (5) defined a parameter, S, equal to the ratio of the specimen diameter to the average planar grain size and showed that the transition temperature increases with increases in S, Figure 1. Therefore, for a constant specimen diameter, their data supports the anomalous observations. However, Cairns and Grant (9) reported the more usual decrease in transition temperature with a decrease in grain size.

**Effects of interstitials on the transition temperature**

The work reviewed by Edwards et al. (2) showed the possible drastic effects of interstitials on the brittle-ductile transition temperature. More recently the specific effects of increasing the amount of carbon, oxygen and nitrogen over the levels of high purity iodide chromium have been investigated (9,11,14,18). Allen et al. (11) found that 100 to 200 ppm carbon or oxygen increases the transition temperature of
Figure 1. Size effect on the tensile transition temperature of recrystallized chromium (5)
wrought chromium 30 to 190°C, and recrystallized chromium 200°C. The effect on quenched material is greater than on furnace cooled, and carbon has a greater effect than oxygen. The results of Cairns and Grant (9), summarized in Table 2, emphasize the importance of the cooling rate after recrystallization.

Table 2. Effects of interstitials on the transition temperature (9)

<table>
<thead>
<tr>
<th>Interstitial</th>
<th>Thermal history</th>
<th>Concentration change, ppm</th>
<th>Transition temperature change, °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>N</td>
<td>slow-cooled</td>
<td>3-200</td>
<td>135-182</td>
</tr>
<tr>
<td></td>
<td>hot-oil-quenched</td>
<td>3-500</td>
<td>250-390</td>
</tr>
<tr>
<td></td>
<td>water-quenched</td>
<td>3+70</td>
<td>250-520</td>
</tr>
<tr>
<td>C</td>
<td>slow-cooled</td>
<td>3+500</td>
<td>135-177</td>
</tr>
<tr>
<td></td>
<td>hot-oil-quenched</td>
<td>3+200-500</td>
<td>250-400-400</td>
</tr>
<tr>
<td>O</td>
<td>slow-cooled</td>
<td>25+200-1000+1700</td>
<td>135+165+140+220</td>
</tr>
<tr>
<td></td>
<td>hot-oil-quenched</td>
<td>25+180-400+1700</td>
<td>250+430+340+340</td>
</tr>
</tbody>
</table>

Solie and Carlson (14) observed the effects of added nitrogen on the transition temperature of both single crystals and polycrystalline iodide chromium. They found that increasing the nitrogen concentration of single crystals increases the transition temperature of furnace-cooled specimens more than oil-quenched specimens - the reverse of polycrystalline behavior. The effect of aging time at 200°C on the transition temperature of single crystals and polycrystalline material containing 225 and 125 ppm nitrogen, respectively, was
determined. During the first 40 minutes of aging the polycrystalline material shows a sharp decrease in transition temperature while the transition temperature of the single crystals remains constant. On continued aging the transition temperature of both crystalline states increases with time.

The work just mentioned emphasizes the dependence of the brittle-ductile transition temperature on interstitial content, particularly nitrogen, and on thermal history. Weaver (18) further elucidated this dependence by studying the changes in resistivity and hardness of oil-quenched chromium-nitrogen alloys during aging at 150 to 400°C. He assumed a very rapid initial rise in resistance was due to nucleation. Aging of a 110 ppm nitrogen alloy is depicted in Figure 2. The initial rise is too rapid at temperatures greater than 100°C to be shown in the figure. Hardness increases on aging were found to correspond to the decreases in resistance. The kinetics of the process can be represented by Zener's equation \( W = kt^n \) with \( n = 1.38 \), close to the value of 1.5 predicted for a precipitate growing equally in all directions. An Arrhenius plot yields an activation energy of 17.8 kcal/mole. By preaging at 125°C, to establish a constant diffusion path length, followed by aging at higher temperatures this value is increased to 25.7 kcal/mole, closer to the value found by internal friction methods for the diffusion of nitrogen in chromium.

Most of the explanations of the effects of nitrogen on the transition temperature summarized above, particularly the
Figure 2. Change in resistivity (top) and hardness (bottom) during aging of a Cr-110 ppm N alloy quenched from 1200°C (18)
higher transition temperature of quenched chromium compared to slow-cooled chromium, were based on the assumptions that oil or water quenching was rapid enough to retain all the nitrogen in solution and that nitrogen in solution was more detrimental to ductility than nitrogen present in the form of precipitates. However, the recent work of Klein and Clauer (19) and Gilbert and Klein (20), reported after the current project was in progress, make these assumptions questionable. Klein and Clauer (19) in a study of internal friction found that it is necessary to quench 47 mil wire directly into water to retain all the nitrogen in solution in a material that contains only 4 ppm nitrogen. Furthermore, increasing the nitrogen concentration increases precipitation kinetics. Gilbert and Klein (20) determined that a cooling rate of approximately 9000°C per second is necessary to retain all of 26 ppm nitrogen in a solution. A rate of 40°C per second retains only 6 out of 26 ppm, while a rate of 0.09 degrees per second retains less than 1 ppm. They also measured the transition temperature of chromium containing 26 ppm nitrogen and found that quenching at a rate of 9000°C per second produces a material with a transition temperature about 74°C lower than aged material—the reverse of all previous findings. They concluded that nitrogen in solution is less detrimental to ductility than nitrogen present as a precipitate, and that most quenching and aging experiments performed prior to their work actually involved a modification in a preexisting precipitate.
Certainly none of the other work reviewed here approached the cooling rates apparently required to prevent precipitation. Comments on the mechanical studies of the transition temperature

In considering the relationship of various parameters to the brittle-ductile transition temperature several observations can be made. The similarity between the temperature dependence of the yield stress in compression and fracture stress in tension implies that the fracture controlling mechanism is closely related to the yield phenomena. Further evidence of this will be discussed shortly. Because of this close relationship the cause of the transition may change if the temperature at which the transition occurs is changed from one region of yield behavior to another. For example, a change in grain size or specimen geometry as well as interstitial content could cause a shift in transition temperature from a region of high interstitial mobility, the strain aging region, to a lower temperature at which the interstitials were quite immobile.

Most of the current hypotheses concerning the effect of nitrogen on the transition temperature assume nitrogen is retained in solution by quenching at normal rates. However, both the yield point phenomena and the prestrain effects can be explained by a model based on grain boundary penetration by slip bands rather than a model based on dislocation locking by interstitials. This diminution of the importance of intersti-
tial nitrogen combined with the inability of chromium to retain a large amount of nitrogen in solution upon quenching makes an explanation of the effects of cooling rates on the transition temperature based only on changes in the amount of interstitial nitrogen untenable. A new model has not been proposed although Gilbert and Klein (20) have suggested that a change in precipitate morphology is responsible. Further progress toward an acceptable hypothesis seems to require more information on the microstructure of the metal. The presently available information will be surveyed in the following sections.

Microstructural Observations

**Interstitial nitrogen and chromium nitrides**

The solubility of nitrogen in chromium has been determined by internal friction measurements and diffusion couples (21,22). Klein and Glauber (19) found that the solubility of nitrogen at 900°C was only 32 ppm, decreasing to about 1 ppm at 500°C. Their data fit the empirical relation

$$\log \text{wt.}\% \text{ N} = -\frac{4130}{T} + 1.05$$

which gives a value of about $10^{-9}$ ppm for room temperature. The pressure-temperature relations of the chromium-nitrogen system have been determined by Sano (23).

Two nitrides of chromium have been identified (24), hexagonal Cr$_2$N and face centered cubic CrN. Servi and Forgeng (25) heated electrolytic chromium flakes in argon containing
a trace of nitrogen at 1500°C for 30 hours followed by furnace-cooling. Nitrides were formed on the surface, in the grain boundaries, and within the grains. The precipitate was extracted with a bromine-methanol solution and identified by x-ray and electron diffraction as Cr$_2$N and CrN. They concluded that Cr$_2$N formed at 1500°C and that the surface of the Cr$_2$N layer was partially transformed to CrN, which is stable at low temperatures, during cooling.

Yoshida et al. (26) used electron transmission to study the effect of heat treatment and working on chromium containing 40 ppm nitrogen. They found that oil quenched material contained small spots in the matrix (10 to 100Å in diameter), but no other precipitate in the grain boundaries or matrix. Both air-cooled and furnace-cooled specimens contained not only the spots, but also platelets (discs or ribbons). After aging for 15 minutes at 500°C most of the spots disappeared. No coherency strains were observed. Some of the precipitates were on dislocations and some dislocation loops were observed around others. Precipitation on grain boundaries occurred during deformation. Although no diffraction patterns were obtained from any of the precipitates, the authors concluded that the spots were isomorphous with the platelets, and the platelets, the habit planes of which were \( \{100\} \), were assumed to be Cr$_2$N.

**Oxides**

Oxygen has a very low solubility in chromium and is
usually present as a randomly distributed, globular oxide which is very stable. Although Cairns and Grant (9) assumed they could retain 200 ppm oxygen on quenching in hot oil from 1200°C, there is little other evidence indicating that much importance can be attributed to precipitation after quenching. However, stable oxides on grain boundaries may be important during crack initiation. Hook et al. (27) associated an idiomorphic cubic phase with the nucleation of intergranular cracks. In a subsequent study by Hook et al. (28) some Cr₂O₃ was found to form intergranularly at temperatures above 1300°C and Cr₃O₄ above 1500°C.

Fracture Mechanisms

The question of whether fracture in chromium is controlled by crack initiation or propagation has not been unequivocally resolved. The hypothesis that crack propagation controls fracture is supported by evidence that significant plastic deformation accompanies brittle cleavage (15,29), comparison of single crystal and polycrystalline behavior (4), and under special conditions the presence of nonpropagating microcracks below the transition temperature (15). A number of the specific mechanisms which have been postulated to explain fracture on the basis of crack propagation control have involved interstitials or precipitates. Most of the arguments based on interstitials assumed that Cottrell locking is an important factor in yield behavior, but this has been shown not to be
true in all cases (3). It has been proposed that precipitates both generate (14) and hinder (29, 14) the motion of dislocations moving under the stress field of the crack, in either case controlling the plastic deformation which tends to blunt the tip of the crack and impede its progress. Alternatively, crack nucleation by large precipitates has also been suggested (14).

The extreme notch sensitivity of chromium suggests crack initiation control of fracture. In the absence of surface flaws the proponents of an initiation controlled brittle-ductile transition in polycrystalline chromium espouse the idea of a crack resulting from slip blockage by a grain boundary followed by transgranular cleavage (6, 9, 23, 5, 27). They note that in those cases where a source of fracture could be identified, the source was either in a grain boundary or on a smooth cleavage facet near a grain boundary (5, 6, 27, 28). It has been suggested that precipitates in the grain boundaries nucleate the cracks (27, 28). No correlation was found between the cause of crack initiation and interstitial content (6).

Crack nucleation by twinning has been observed (3); however, since twinning in low nitrogen chromium occurs below −150°C and the addition of nitrides suppresses twinning to even lower temperatures, this source of fracture is not considered to be relevant to the current study.
EXPERIMENTAL PROCEDURES

The four point bend test rather than a tensile or notched impact test was employed to determine the brittle-ductile transition temperatures because it minimized the problems of specimen preparation while at the same time yielding sufficient information on the fracture process for interpretation. The bend test results were supplemented by resistance ratio and hardness measurements and correlated with the microstructures of the alloys.

Sample Preparation and Heat Treatment

The chromium in this study was produced by the Chromalloy Corporation using the iodide process. A typical analysis furnished by the supplier was: 3 ppm aluminum, 1 ppm calcium, 0.3 ppm copper, 10 ppm iron, 0.1 ppm magnesium, 0.1 ppm nickel, 10 ppm silicon, 1 ppm vanadium, 6 ppm oxygen, 0.2 ppm hydrogen, 1 ppm nitrogen and 10 ppm carbon. Analysis by the spectrographic and chemical analysis groups of the Ames Laboratory after the specimens had been fabricated revealed that the only increases in impurities were in oxygen, to about 50 ppm, and in nitrogen, which varied from 3 to 20 ppm.

All specimens were fabricated in the same manner to the same dimensions, suitable for bend tests, whether they were actually used in bend tests or for other measurements. Thus any mechanical variables in preparation were minimized, and the same nitrogen charging techniques could be used for all
the alloys. Arc-melted billets were welded into stainless steel jackets and rolled at 900°C. The same rolling schedule was used for all the billets to insure a uniform grain size. The resulting bars were recrystallized by annealing in a vacuum for one hour at 1100°C, and specimens were cut from them perpendicular to the direction of rolling. The specimens at this stage in their preparation were 1 x 0.25 x 0.050 inches.

Grain size determinations were made on specimens from each bend test series by the linear intercept method in both the width and thickness directions of the finished specimens, i.e. vertically perpendicular to the direction of rolling and in the direction of rolling, respectively. The mean grain diameters in the thickness direction were between 0.071 and 0.126 mm. The mean grain diameter in the width direction was approximately 12% smaller than in the thickness direction. The grain sizes in both directions were within the range which Hook and Adair (5) found to have the least effect on the transition temperature. The slight variations in grain size in this study had no detectable effect on any of the properties measured.

Since the working characteristics of chromium may be a function of nitrogen concentration, nitrogen was added to the specimens after the fabrication and recrystallization steps rather than during melting. This procedure avoided the possi-
bility of different nitrogen concentrations having an effect on the final grain size of the specimens. Nitrogen charging was accomplished by holding the specimens in a purified nitrogen or anhydrous ammonia atmosphere for two hours at the required temperature, corresponding to the desired concentration on the solvus line, followed by a 48 hour anneal at the same temperature in an argon atmosphere. X-ray diffraction data showed that the layer of nitride formed during charging was Cr$_2$N which agrees with the findings of Sano (23). Equilibrium was established between the Cr$_2$N phase and nitrogen in interstitial solution during the annealing period, and the desired concentrations of nitrogen were obtained by selecting an annealing temperature between 950 and 1150°C. Complete homogenization was demonstrated at several nitrogen concentrations by analyzing half of a specimen at full thickness and only the core of the other half.

The homogenized specimens were then transferred to a vertical quenching furnace and, after holding them for an additional two hours at the annealing temperature, they were quenched directly into mineral oil. A 0.002-inch layer containing the excess Cr$_2$N was then removed from the specimens by grinding. Most of the aging was done in an argon atmosphere in a preheated furnace. Sufficient time was allowed for the specimens to come to temperature and after aging they were allowed to furnace cool. Unless specifically stated otherwise, the specimens were held at temperature for ten minutes
for aging temperatures of 300°C or above and 7½ hours for aging at 150°C. Weaver’s data, Figure 2, indicates these aging periods are sufficient for complete precipitation. The aging temperatures reported are accurate to within ± 5°C. Following the heat treatment another 0.001 inch layer was removed by grinding, and the specimens electropolished in methanol-10% perchloric acid at -60°C to a final thickness of 0.0400 ± 0.0005 inches.

The possibility of aging at room temperature occurring between the time the specimens were quenched and subsequently aged was examined by periodically measuring the resistance ratios of material containing 20 and 350 ppm for six weeks after quenching. The ratio remained constant throughout this period for both concentrations. None of the specimens were held any longer than four weeks between quenching and aging. A spot check of several aged specimens from other experiments at various intervals up to one year after initially measuring the ratio showed no change, thereby establishing the stability of the aged condition at room temperature.

Bend Tests

A four-point bend test was used to determine the brittle-ductile transition temperature because the constant bending moment which is applied between the center loading points provides more information than a three-point loading in which there is no area of constant moment. In four-point loading
one is able to measure, at least in the elastic range, the bulk property of a metal under a determinable stress; whereas, in the case of three-point loading, only a single line is under the maximum stress, resulting in a very complex state of stress. The apparatus, shown in Figure 3, was designed to approximate as closely as possible a state of pure bending in the specimen so that a uniaxial stress was created. The critical dimensions are the spacings of the 1/8 inch diameter hardened steel pins. The inside pins are 90 mm apart and the outside ones 185 mm.

Tests were run on a Riehle Universal Screw Power Machine, Model FS-10, and both applied load and deflection were continuously recorded. Deflection of the specimen was measured relative to a line through the center load points, i.e. relative to the moving member. A maximum deflection of slightly over 0.030 inches was possible before binding in the apparatus occurred. The extension arm which was attached to a standard deflectometer is shown at the right of Figure 3. All tests were run at a crosshead speed of 0.005 inches per minute. In operation the bending apparatus was submerged in a vigorously stirred constant temperature bath of methanol cooled to the desired temperature by regulating the flow of liquid nitrogen through a copper coil. The temperature was maintained constant within ±0.5°C, and specimens were held at the desired temperature for 10 minutes prior to testing.

The brittle-ductile transition temperature is an arbi-
Figure 3. The four-point bend test apparatus
trarily defined parameter which usually denotes the change between ductile and cleavage modes of failure. It has been variously defined as the temperature at the knee, midpoint, or foot of the deflection versus temperature curve or as the temperature at which specimens change from exhibiting a yield point to failure without a yield point. In chromium the transition occurs over a very narrow temperature range and consequently there is little difference between these various definitions. Since the precision with which the transition temperature in this study was determined varied from one series of alloys to another, the transitions are represented as a range of temperatures in this work. The range was determined by the highest temperature at which a specimen exhibited no yield point and the lowest temperature at which yielding was observed. If this range was three degrees or less, only the mean value was used. In most cases this range was the same as that based on a criterion of deflection greater or less than 0.0015 inches, or one based on a criterion of no measurable plastic deflection or the maximum deflection the bend test apparatus would allow. In a few series, although specimens tested above the transition temperature did deflect a significant amount after yielding, none could be deflected a full 0.030 inches.

In most cases there was little difference between upper and lower yield stresses, indeed, no load drop was noted for many specimens. In plots of load versus temperature for
individual transition temperature determinations more scatter was observed in the upper yield stress than in the lower yield stress, as has been observed previously (3). In a few cases the lower yield stress could not be determined due to premature failure shortly after the upper yield. In all cases the transition temperature fell in the region in which the yield stress was very nearly a linear function of temperature. A typical plot of yield load as a function of temperature is shown in Figure 4 with the corresponding data for deflection as a function of temperature.

Supplementary Procedures

Standard metallographic techniques were employed. Murakami's etch was found to be effective in disclosing the precipitates and a 10% oxalic acid electrolytic etch to be best for grain boundaries.

Fracture surfaces were studied with both an electron microscope using carbon replicas of the surfaces and a light microscope. All attempts to relate the precipitates to the fracture surface by extracting the particles with the carbon replicas were unsuccessful even though a variety of etching and replication techniques were employed.

Foils for electron transmission microscopy were prepared by grinding fragments of bend test specimens to a thickness of about 0.003 inches and then thinning them electrolytically in a methanol-10% perchloric acid solution at -60°C. Precipi-
Figure 4. Typical plots of yield load and deflection as a function of temperature
tates were identified and their habit planes determined by selected area diffraction. Precipitate orientation was also determined optically using oriented single crystals. The electron diffraction identification of the precipitates was verified by x-ray diffraction. An arc-cast alloy nominally containing 660 ppm nitrogen was aged at 635°C for 10 hours and then dissolved in a methanol-10% bromine solution. An x-ray diffraction pattern of the residue was obtained by the Debye-Scherrer method.

The ratio of the resistance of specimens at 300°C to that at 4.2°C was determined rather than measuring the absolute resistivities to avoid the problems of precisely measuring the specimen dimensions. Separate electrical connections to the specimen were used for current supply and voltage measurement. The voltage drop at several current settings between 0.2 and 1.0 amperes was measured and the mean value of the calculated resistances used to determine the ratio. Accuracy was estimated to be better than ± 5%.
PRESENTATION OF DATA AND DISCUSSION OF RESULTS

The effects of aging were found to result in two distinct types of behavior. Those alloys aged below 500°C exhibited regular progressive changes in brittle-ductile transition temperature and resistance ratio as a function of nitrogen concentration or aging temperature. However, those aged above 600°C exhibited pronounced extrema in the same properties as a function of nitrogen concentration. The data and discussion will be presented in two parts corresponding to this natural division. A close correlation was found between resistance ratios and transition temperatures that seems to require a mechanism that at least in part accounts for both. Such a model is proposed for both the high and low temperature aging effects and is presented immediately after the data for each part. Neither section implies either a nucleation or propagation control of fracture. However, the possible difference in optimum nitrogen concentration between that required for a minimum in yield stress and for a minimum in transition temperature for aging at high temperature suggests an additional mechanism may be operative. The fractographic studies presented in the third part of this presentation explore this possibility in the light of a propagation controlled mechanism.
Low Temperature Aging

Brittle-ductile transition temperature and resistance ratio determinations

The effects of aging at temperatures of 455°C or below were determined by measuring the transition temperatures and resistance ratios of alloys of several nitrogen concentrations. Figure 5 shows that the aging at low temperatures yields higher transition temperatures than are found for the as-quenched condition at low nitrogen concentrations. The transition temperatures of the aged alloys gradually decrease with an increase in nitrogen concentration while the transition temperatures of the as-quenched alloys remain almost constant. Thus at 675 ppm nitrogen the aged alloys have a lower transition temperature than the as-quenched alloys. It is to be noted that there is little difference between the alloys aged at 152 or 305°C while aging at 455°C always produced the lowest transition temperature.

Alloys of several more nitrogen concentrations were used in resistance ratio studies than in transition temperature determinations (Figure 6) and an apparent minimum as a function of concentration was found for all aging conditions except prolonged aging (14 hours) at 455°C. The progressive increases with aging temperature are similar to those noted by Weaver (Figure 2). Table 3 demonstrated that overaging was not observed after prolonged aging at either 152 or 305°C.
Figure 5. Transition temperatures of as-quenched alloys and alloys aged at low temperatures as a function of nitrogen concentration.
Figure 6. Resistance ratios of as-quenched alloys and alloys aged at low temperatures as a function of nitrogen concentration.
Table 3. The effect of time on the resistance ratios of aged chromium alloys

<table>
<thead>
<tr>
<th>Nitrogen concentration</th>
<th>Aging temperature</th>
<th>Aging time</th>
<th>Resistance ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>3 ppm</td>
<td>152°C</td>
<td>3 hr</td>
<td>58</td>
</tr>
<tr>
<td></td>
<td></td>
<td>50 hr</td>
<td>63</td>
</tr>
<tr>
<td></td>
<td>305°C</td>
<td>10 m</td>
<td>94</td>
</tr>
<tr>
<td></td>
<td></td>
<td>7 hr</td>
<td>98</td>
</tr>
<tr>
<td>210 ppm</td>
<td>152°C</td>
<td>3 hr</td>
<td>36</td>
</tr>
<tr>
<td></td>
<td></td>
<td>50 hr</td>
<td>37</td>
</tr>
<tr>
<td></td>
<td>305°C</td>
<td>10 m</td>
<td>52</td>
</tr>
<tr>
<td></td>
<td></td>
<td>7 hr</td>
<td>55</td>
</tr>
<tr>
<td>575 ppm</td>
<td>152°C</td>
<td>3 hr</td>
<td>39</td>
</tr>
<tr>
<td></td>
<td></td>
<td>50 hr</td>
<td>31</td>
</tr>
<tr>
<td></td>
<td>305°C</td>
<td>10 m</td>
<td>56</td>
</tr>
<tr>
<td></td>
<td></td>
<td>7 hr</td>
<td>52</td>
</tr>
</tbody>
</table>

**Yield properties**

The yield properties of the alloys were compared by selecting an arbitrary temperature of -30°C which came closest to being common to alloys aged at both high and low temperatures. Where necessary the yield load versus temperature data was extrapolated to this temperature. In Figure 7 the yield load at -30°C is plotted as a function of transition temperature to show that in general the transition temperature decreases as the yield stress decreases for the alloys aged at low temperatures. It should be noted that the yield strength of the aged alloys is greater than that of the as-quenched alloys. There is no apparent correlation between nitrogen
Figure 7. Yield loads of as-quenched alloys and alloys aged at low temperatures as a function of transition temperature.
concentration and yield strength for the as-quenched alloys. The yield strengths of the alloys aged at low temperature vary with nitrogen concentration in a manner similar to the transition temperatures although there is little difference in yield strength between the three aged conditions.

**Hardness**

All alloys aged at low temperatures for the normal periods of time used in this investigation are harder than the as-quenched alloys. Both the as-quenched and aged alloys exhibit a maximum in hardness as a function of nitrogen concentration at about 160 ppm, which corresponds to the minimum observed in the resistance ratios. Furthermore, aging at 305°C yields a harder material than either 152 or 455°C aging. Prolonged aging (14 hours) at 455°C produces an overaging effect similar to that observed in a 110 ppm alloy by Weaver (Figure 2). The hardness of the overaged alloys approaches that of alloys aged at high temperature as represented in Figure 8 by those aged at 635°C.

**Microstructures**

Chromium containing 20 ppm nitrogen has only a few precipitates that are visible at a magnification of 1400 (Figure 9). The microstructure of this alloy does not change noticeably on aging for the normal periods of time used in this investigation; however, after prolonged aging at 455°C the amount of precipitate increases as shown in Figure 10. Any
Figure 8. Hardness of as-quenched alloys and alloys aged at low temperatures as a function of nitrogen concentration
Figure 9. 0r-20 ppm N, as-quenched, showing a few nitride precipitates. Murakami's etch. X1400

Figure 10. Or-20 ppm N, aged 14 hours at 455°C, showing an increase in the density of Type I precipitates. Murakami's etch. X1400
changes in precipitate density which might occur during prolonged aging would be more difficult to detect at higher nitrogen concentrations because it would be masked by the greater amount of precipitate formed during quenching (Figure 11).

Chromium nitride particles all having similar morphology (referred to as Type I) were visible at a magnification of 1400 in alloys containing up to 350 ppm nitrogen. As shown in Figure 10 this "crowsfoot" precipitate appears to have grown in three directions from a single point on well defined crystallographic planes. A 675 ppm nitrogen alloy (Figure 12) also contains Type I precipitate, but a second form (referred to as Type II) is predominant. Type II, which has a rod or platelet shape, appears to have grown with a more random orientation. Precipitation in the grain boundaries is apparent in a 350 ppm alloy and is more extensive in the 675 ppm nitrogen alloy.

Both Types I and II were identified as hexagonal Cr₂N by electron and x-ray diffraction. The details of these identifications are presented in the appendix. The habit plane of Type I is \{100\}_α while that of Type II is \{112\}_α.

Although a detailed electron microscopic study of all the alloys was not made, observations incidental to the identification of Type I and II precipitates by electron diffraction supported the findings of Yoshida et al. (26). That is to say, the alloys aged at the lower temperatures (up to 450°C)
Figure 11. Cr-165 ppm N, aged at 305°C, showing Type I precipitate and clean grain boundaries. X1400. Murakami's etch

Figure 12. Cr-675 ppm N, aged at 305°C, showing predominantly Type II precipitate within the grains and a nitride precipitate in the grain boundaries. X1400. Murakami's etch
contained dot-like precipitates, while those aged at temperatures above 600°C in general did not. This contrast is illustrated in Figure 13.

Discussion of low temperature aging

As-quenched alloys As-quenched alloys are characterized by an apparent minimum in the resistance ratio and a maximum in hardness while the transition temperatures and yield strength appear to be independent of nitrogen concentration. Type I precipitate is observed in the 20 ppm nitrogen alloy and increases in density with nitrogen concentration. Type II is also observed at the higher concentrations. From these observations it is concluded that the Type I and II precipitates that form during quenching are incoherent, otherwise the cumulative effects of the lattice strain would produce a monotonic increase in hardness with nitrogen concentration.

By comparing the quenching rate used in this study with the data reported by Gilbert and Klein (20) it is estimated that 8 to 10 ppm of nitrogen is retained in solution. This assumption is further supported by the similarity between this study and Weaver's (18) with regard to resistance data at low aging temperatures. The quenching rate used by Weaver was only slightly faster than that used in this study. Furthermore, comparison of Weaver's kinetics and Gilbert and Klein's internal friction results show that Weaver was in fact following a precipitation process. The minimum in the resistance ratio as a function of nitrogen concentration suggests that
Figure 13a. Cr-350 ppm N, aged at 152°C, showing large Cr$_2$N and small dot-like particles. X45,000

Figure 13b. Cr-325 ppm N, aged at 750°C, showing large Cr$_2$N precipitates but no small dot-like particles. X38,000
all of the nitrogen in the 3 ppm alloy was retained in solution after quenching and that the amount retained gradually increases up to the overall nitrogen concentration corresponding to the minimum in the resistance ratio and then again declines somewhat. This implies that solution hardening then accounts, at least in part, for the peak in hardness in the as-quenched curve.

The assumptions made above do not preclude the possibility of a small amount of coherent precipitate being formed during quenching such as the tiny "dot-like" precipitates noted by Yoshida et al. (26). The existence of such a precipitate in the as-quenched state and its subsequent removal by aging at high temperatures could explain at least in part the fact that for all nitrogen concentrations the as-quenched alloys are harder than alloys aged at 635°C as is shown in Figure 8.

**Effects of aging at low temperatures**

Aging at low temperatures produces an increase in yield strength and a progressive increase in resistance ratio with aging temperature for all alloys. However, there is a maximum in hardness as a function of concentration at about 160 ppm and, for alloys of any given concentration, as a function of aging temperature at about 305°C. The hardness values decline with overaging at 455°C to values approaching those characteristic of high temperature aging, and this prolonged aging is necessary to cause any change in the density of Type I
precipitates compared to the density in the as-quenched state.

Model  A model is postulated to explain some of the effects of aging based on the morphology of precipitates formed during quenching and on the precipitation of nitrogen retained in solution after quenching either on pre-existing precipitates or as new particles which may undergo further changes on continued aging. It is felt that the low temperature aging effects can be explained in the following way. At low nitrogen concentrations it is assumed that most of the nitrogen retained in solution after quenching precipitates as new coherent or semicoherent particles, similar to the dot-like particles of Yoshida (26). As the aging temperature increases from 152 to 305°C, larger coherent particles result due to the higher mobility of the nitrogen and the lower nucleation rate. This incremental change in the particle size is accompanied by increases in lattice strain relative to the as-quenched condition. However, aging at 455°C produces particles which are sufficiently large to be only semicoherent and the lattice strain diminishes. As the nitrogen concentration increases up to about 160 ppm it is postulated that the increased amounts of nitrogen retained in solution after quenching produce more new coherent or semicoherent particles upon aging so that the cumulative lattice strain per unit volume becomes greater. However, as the density of Type I and, at higher concentrations, Type II precipitates formed during quenching increases it seems reasonable to assume that
more and more of the retained nitrogen would precipitate on the pre-existing particles, rather than form new particles. Therefore, since there are relatively fewer new particles formed at higher concentrations, the total lattice strain decreases. The effects of overaging at 455°C are similar to the effects of aging at high temperature and can more clearly be discussed in that context.

**Explanation of hardness changes** The effects of low temperature aging are most evident in the hardness data. The increase in hardness over the as-quenched condition is the result of the precipitation of retained nitrogen as coherent and semicoherent particles. Aging at 305°C produces the highest hardness values at a given nitrogen concentration because the particles produced by aging at this temperature have a greater lattice strain associated with them than the strain associated with the particles produced by aging at either 152 or 455°C. The peak in hardness as a function of concentration reflects the maximum amount of nitrogen retained in solution on quenching, while the diminishing effects of aging on hardness at high concentrations occurs because there are relatively fewer precipitates formed at high concentrations due to the absorption of supersaturated nitrogen by pre-existing particles.

**Explanation of resistance ratios** The absence of an exact correlation between the effects of aging on resistance ratios and hardness values indicates that somewhat different
factors are influencing these properties. The increase in resistance ratios that results from the precipitation of the nitrogen retained in solution after quenching exceeds any decrease that might arise due to coherency strains associated with the new particles. If this were not the case, the ratios of the aged alloys would be lower than those of the as-quenched alloys. Furthermore, lattice strains apparently do not control the differences in ratios that result from the different aging treatments, otherwise aging at 305°C would have been expected to produce the lowest ratio, similar to the effect on hardness. A more important effect, therefore, of the changing precipitate distribution may be its effect on the scattering of electrons by the particles in the manner proposed by Mott and also suggested for this case by Weaver (18). This assumption implies that the particles formed during quenching must be closest to the critical size, and that as the aging temperature is increased the size progressively digresses from the critical one.

**Effect on transition temperatures** The changes in transition temperature are apparently due to a complex interaction of several factors. There are correlations between the transition temperatures and both hardness values and resistance ratios. Thus the increasing lattice strain at low nitrogen concentrations which results in a greater hardness may also account for a higher transition temperature relative
to the as-quenched condition. Moreover, not only does aging at 455°C produce the softest alloys, but it also produces alloys with the lowest transition temperatures. The trends in transition temperatures and resistance ratios with nitrogen concentration for aging at 152 and 305°C are also similar. However, the incremental changes in hardness diminish with increasing nitrogen while those in transition temperature remain relatively constant in a manner similar to the incremental changes in resistance ratio. The yield strength reflects the same changes, but with less sensitivity.

High Temperature Aging

Brittle-ductile transition temperature and resistance ratio determinations

The transition temperatures and resistance ratios of a number of alloys of different nitrogen concentrations were determined after a double-aging heat treatment. A primary aging (originally intended as a nucleation step) at various temperatures below 500°C for 2 to 18 hours was followed by aging at 635°C for 2 to 10 hours. The primary aging time was varied with temperature to insure complete precipitation. The purpose of the secondary aging was to establish as much as possible a matrix in which the amount of residual nitrogen in solution was constant and in which the differences in lattice strains created during cooling were minimized. It was felt that in this way the effects of the nitrides as a function of
volume fraction and distribution could best be studied independently of other variables. The results are shown in Figures 14 and 15 including those for the as-quenched alloys for comparison.

The significant feature of these figures is the decrease in transition temperature with increasing nitrogen concentration up to about 350 to 400 ppm. An increase in nitrogen above this level reduces the ductility. The resistance ratio data follows a similar trend, but apparently peaks at a slightly lower concentration of nitrogen, 250-300 ppm. This behavior is quite different than the more commonly reported continuous increase in transition temperature with increasing nitrogen concentration found for recrystallized chromium.

Included in Figures 14 and 15 are the data for aging at 635°C for 2 to 10 hours without a primary aging. Comparison with the double-aged alloys demonstrates that primary aging has little effect on either the transition temperature or the resistance ratio. This is not too surprising in view of the knowledge, which became available after this series of experiments was begun, that the quenching rate employed in these experiments was sufficient to retain only a small fraction of the nitrogen in solution. Subsequent examination of the microstructures showed that precipitates were, in fact, present in the as-quenched condition of all of the alloys.

**Yield properties**

As with low temperature aging a temperature of -30°C was
Figure 14. Transition temperature as a function of nitrogen concentration for alloys aged at high temperatures
Figure 15. Resistance ratios as a function of nitrogen concentration for alloys aged at high temperatures.
selected for comparing the yield behavior of the various alloys. The yield load at this temperature for alloys aged at 635°C (Figure 16) appears to have a relationship to nitrogen concentration similar to that observed for ductility; however, there is a little more scatter in the data for the double-aged alloys (Figure 17). All of the yield loads at -30°C were between 55 and 100 lbs. This corresponds to a range of maximum fiber stress at the yield point, assuming elastic behavior, of 61 to 136 ksi. Marcinkowski and Lipsitt (35) report a value of about 52 ksi for the lower yield stress at -30°C for recrystallized, unalloyed chromium with a mean grain diameter of 0.1 mm. This compares favorably, considering the increase in yield stress for a bend test relative to a uniaxial compression test, with the value of 85 ksi for unalloyed chromium aged at 635°C found in this study.

**Hardness**

In contrast to the above correlations between concentrations and transition temperature, resistance ratio, or yield stress, the hardness of the alloys increases very slightly with nitrogen concentration (Figure 8). As is also seen from the figure, the hardness of the alloys in the as-quenched condition is slightly greater than after aging at 635°C. The hardness values of the double-aged alloys and those with a low nitrogen concentration aged for only a short time were virtually coincident with those of the alloys fully aged at 635°C and so for clarity are not shown in the figure.
Figure 16. Yield load as a function of nitrogen concentrations for alloys aged at 635°C.
Figure 17. Yield load as a function of nitrogen concentration for double-aged alloys
Kinetics

Although a detailed kinetics study of the changes occurring during aging was not attempted, a few experiments were made in which only resistance ratios were used to follow the progress of aging at 635°C as a function of time. Figure 18 shows that the ratios apparently increase to a constant value for alloys containing 280, 350, and 660 ppm nitrogen. Again the effect of concentration is noted - the ratio of the 350 ppm nitrogen alloy being higher than either of the other two. At lower nitrogen concentrations maxima in transition temperatures and resistance ratios were found at short aging times as shown in Figures 19 and 20. Similar behavior in transition temperatures was reported by Solie and Carlson (14) for an alloy containing 125 ppm. It is felt that the ratios at shorter times were much higher; however, because of the time required to bring the specimens to temperature, study of shorter times was not feasible.

To determine whether or not the optimum in mechanical properties is obtained with aging at 635°C, an alloy containing 325 ppm nitrogen was aged at 750, 855, and 945°C. Referring back to Figures 14 and 15, no significant change relative to the 635°C heat treatment was found. As is seen from these figures some overaging was observed in an alloy containing 675 ppm nitrogen aged at 945°C compared to the 635°C aging.

Microstructure

Chromium containing 20 ppm nitrogen contains only a few
Figure 18. Resistance ratios as a function of aging time at 635°C for three Cr-N alloys.
Figure 19. Transition temperature as a function of aging time at 635°C for a Cr-20 ppm N alloy.
Figure 20. Resistance ratios as a function of aging time at 635°C for Cr-20 ppm N and Cr-215 ppm N alloys
Type I precipitates in the as-quenched condition as shown in Figure 9. After being aged for 10 minutes at 635°C the density of precipitates is somewhat greater (Figure 21), and finally Figure 22 shows the microstructure of the fully aged alloy. This change in precipitate density with aging time is more difficult to detect at higher concentration of nitrogen because of the greater amount of precipitate formed during quenching.

The microstructures of the double-aged alloys and the alloys fully aged at 635°C and above are very similar at comparable nitrogen concentrations. At low nitrogen concentrations only Type I precipitate is present and there is virtually no precipitate in the grain boundaries (Figure 22). As the nitrogen concentration increases the density of precipitates increases, but the size of the individual particles does not grow appreciably. When the nitrogen concentration exceeds about 200 ppm Type II precipitate begins to appear and precipitation in the grain boundaries is evident (Figure 23). At concentrations corresponding to the lowest transition temperatures Type II precipitate is still the minor constituent as seen from Figure 23. Type II precipitate becomes predominant at higher nitrogen concentrations coincident with the increase in transition temperature (Figure 24); however, some Type I precipitate is present in all microstructures. Aging an alloy of intermediate composition at higher temperatures did not result in any noticeable change in microstructure.
Figure 21. A Cr-20 ppm Ni alloy aged at 635°C for 10 minutes showing an increase in the density of Type I precipitates over the as-quenched condition. Murakami's etch. X1400

Figure 22. A double-aged Cr-20 ppm Ni alloy showing Type I precipitates and clean grain boundaries. Murakami's etch. X1400
Figure 23. A double-aged Cr-295 ppm N alloy showing Type I, and some Type II precipitates as well as grain boundary precipitate. Murakami's etch. X1400

Figure 24. A double-aged Cr-652 ppm N alloy showing predominantly Type II precipitates, some Type I, and grain boundary precipitates. Murakami's etch. X1400
As was previously noted and illustrated in Figure 13 a small dot-like particle that is present in alloys aged at low temperatures has for the most part disappeared from alloys fully aged at 635°C or above.

Discussion of high temperature aging

**Effects**

The effects of aging at high temperatures are a function of both time and nitrogen concentration. Consider first the effect of concentration on the stable state achieved after aging. A minimum in the transition temperature occurs at about 350 ppm nitrogen while the yield strength exhibits a minimum at about 250 ppm. The maximum in resistance ratio is rather poorly defined, but appears to fall between 250 and 350 ppm nitrogen. The hardness values are slightly lower in the aged than in the as-quenched condition and are almost independent of nitrogen concentration.

Next consider the effects of aging for a short time at 635°C. For nitrogen concentrations of less than about 250 ppm the resistance ratio increases drastically within a very short time and then gradually declines to a stable value. This decline is accompanied by the appearance of new Type I precipitates in the microstructure. As stated in the preceding paragraph, the final value of the resistance ratio increases with increasing nitrogen concentration. For concentrations greater than 250 ppm the resistance ratios simply level off after the initial rise. No changes in hardness at short aging times were noted.
Finally consider the effects of aging at temperatures greater than 635°C. No change in transition temperature or resistance ratio occurs with a concentration of 350 ppm nitrogen; however, small changes were noted at 575 ppm.

Model  The model proposed to explain some of the effects of aging is extended here to include aging at high temperatures. It is postulated that at total nitrogen concentrations below about 250 ppm the nitrogen retained in solution upon quenching precipitates rapidly as small incoherent particles similar to those formed at 455°C, but having virtually no strain associated with them. This is indicated by the absence of any significant hardness changes from the as-quenched condition. At longer aging times these particles dissolve and the microstructures show that new Type I precipitates have formed. As the nitrogen concentration increases, the density of Type I and, at higher concentrations, Type II precipitates formed during quenching becomes greater thus increasing the probability that nitrogen atoms in supersaturation will diffuse to and precipitate on pre-existing nitride particles rather than forming new ones. It seems reasonable to assume that Type I precipitates control the behavior of the fully aged alloys below about 300 ppm nitrogen and that Type II precipitates gradually become dominant above this concentration.

Resistance ratio effects  In contrast to the low temperature aging, it is the resistance ratios which are most
sensitive to the effects of aging at high temperature rather than hardness values. The high resistance ratios of the low nitrogen alloys after short periods of aging (Figure 20) is interpreted as resulting from the precipitation of the retained nitrogen as small incoherent particles which causes an increase in the resistance ratio without producing any hardening effect. The subsequent decrease in resistance ratios with extended aging apparently reflects the growth of the new Type I precipitates at the expense of the incoherent particles. No completely satisfactory explanation has been found for the increase in the resistance ratios of the fully aged alloys (Figure 15) and the diminishing height of the aging peak with increasing nitrogen concentration up to about 250 ppm; however, if associated with the formation of new Type I precipitates, the changes may occur because of the reduction in the amount of this type of precipitate. With nitrogen concentrations greater than 200 ppm the increasing volume of precipitate may account for part of the decrease in resistance ratio (Figure 15). The apparent increase in resistance ratio after aging a 675 ppm alloy at 950°C compared to aging at 635°C suggests that the state achieved after aging alloys of high concentration is not as stable as that achieved with alloys of intermediate concentrations. This behavior may be associated with the Type II precipitate since it is predominant at high concentrations, but is present in insufficient amounts at intermediate concentrations to be noticeable.
Yield properties  The presence of interstitial impurities still in solution contributes to the athermal component of the yield stress. However, in the present case of alloys fully aged at higher temperatures (Figures 16 and 17) an increase in nitrogen concentration results primarily in a change in precipitate morphology and density without any significant increase in the amount of nitrogen retained in solution. Thus it is assumed that the reduction in yield stress is the result of increasing amounts of Type I precipitates, perhaps by serving as sources for dislocations, while the increase in yield stress at higher concentrations is due to the Type II precipitates. The minimum in yield stress appears to be about 100 ppm lower than the minimum in transition temperature and is close to the concentration at which Type II precipitates are first observed.

Transition temperatures  The transition temperatures exhibit a minimum as a function of nitrogen concentration similar to the resistance ratios and yield strength. As is discussed in a later section, the transition temperatures would be expected to be a function of yield strength and in some respects, the same parameters that affect the resistance ratios. However, since the optimum concentration for the transition temperatures is apparently not the same as for yield strength, and may differ from that for resistance ratio (this is difficult to determine since the resistance ratio minimum is poorly defined), the transition temperature may be
a function of other variables as well.

Fractographic Studies

Examination of fracture surfaces of alloys from each bend test series revealed that in all cases fracture had propagated from a single source at or very close to the tension surface of the specimens. When the source could be identified it was found to be at a grain boundary or at a small, smooth, cleavage facet near the juncture of several grains. Propagation of the crack was almost completely transgranular. Therefore, with respect to source and type of propagation, these results are very similar to those of Hook and Adair (5) and Gilbert et al. (6).

Although no correlation between the site of fracture nucleation and microstructure was found, the appearance of the rest of the surface showed small, but progressive changes as a function of nitrogen concentration and heat treatment. In most cases the surfaces were extremely rough which made it very difficult to obtain photographs with a large area in focus. Consequently, changes were much easier to detect while actually observing the specimens through the microscope than in the fractographs.

As-quenched alloys and alloys aged at temperatures below 500°C have similar fracture surfaces which do not change appreciably with either nitrogen concentration or heat treatment. As the nitrogen concentration increases more cleavage
steps appear on the facets, but few of the jogs noted on the steps of the alloys aged at high temperature were found.

The fracture surfaces of alloys aged at 635°C or above and the double-aged alloys are comparable. Figure 25 shows that the cleavage facets change from relatively flat surfaces with straight river patterns at low nitrogen concentrations to much rougher facets with many cleavage steps, each step containing many jogs, at intermediate concentrations. At higher concentrations the cleavage facets were still rough, but the cleavage steps did not have many jogs in them. Figure 26 shows in greater detail the changes in cleavage step appearance.

The appearance and angle of the jogs in the cleavage steps suggests that they may be due to the Type I precipitate (Figure 26). This is more readily apparent in Figure 27 which shows jogs on a cleavage facet. Although no precipitates could be identified by electron diffraction in carbon replicas of the fracture surfaces, it appeared that in many cases precipitates generated cleavage steps or caused jogs in pre-existing steps. An example of jogs apparently caused by precipitates is shown in Figure 28.

General Discussion

The purpose of this research has been to study the effects of changes in chromium nitride morphology and density on the brittle-ductile transition temperature of chromium.
Figure 25. Alloys aged at high temperature showing the progressive change in fracture surface appearance noted in the text. Nitrogen concentrations and transition temperatures are from top to bottom: 560 ppm and 0 to -12°C, 340 ppm and -62°C, 20 ppm and -10°C. X50
Figure 26. Alloys aged at high temperatures showing the progressive change in fracture appearance with nitrogen concentration. Nitrogen concentrations and transition temperatures are from left to right: 20 ppm and -10°C, 320 ppm and -58 to -60°C, 560 ppm and -18°C. Arrows A point to steps and arrows B point to jogs. X500
Figure 27. Cr-320 ppm N, aged at 944°C showing jogs (arrow) on cleavage facet that may have been caused by Type I precipitate, X500

Figure 28. Cr-20 ppm N, aged at 635°C, showing jogs (arrow) on cleavage steps that may have been caused by Type I precipitate, X26,500, carbon replica
This transition may be looked upon, in a very rudimentary manner, as a competition between the nucleation and propagation of a crack and macroscopic plastic flow of the metal. Obviously the effects of aging and nitrogen concentration on the yield stress are of great importance. Consider the equation for yield stress, \( \sigma = \sigma_0 + k_y d^{-\frac{3}{2}} \). Comparison of yield load-temperature plots of the various alloys used in this study showed that only the temperature independent components of yield stress, \( k_y \) and the athermal part of \( \sigma_0 \), are affected by either nitrogen concentration or aging temperature. The athermal component of \( \sigma_0 \) represents the friction stress arising from dispersed impurities, precipitates, and the Snoek effect. Normally an increase in interstitial content increases \( \sigma_0 \), but in the present case it is proposed that such an increase in concentration changes the morphology of the associated precipitates. It seems quite likely, therefore, that the initial decrease in yield stress with increasing nitrogen concentration after aging at high temperatures is associated with the changes in Type I precipitate and the subsequent increase is associated with Type II. It is also possible that the increase at higher nitrogen concentration is due to increases in \( k_y \) caused by the increasing amount of grain boundary precipitate.

The fractographic studies indicate that a minimum transition temperature is achieved when the cleavage facets exhibit river patterns with many steps and jogs. It is possible
therefore that the minimum in transition temperature is a function, at least in part, of the amount of surface energy required for the propagation of a crack. In other words, as the amount of Type I precipitate increases an increasing amount of energy is required to propagate the crack because the precipitates create steps and jogs on the cleavage facets. At higher concentrations the Type II precipitates become predominate and these present less of an impediment to the propagation of the cracks, as evidenced by the reduction in the number of jogs on the steps. The different effects produced by the two precipitates may be due to their different habit planes. Type I, with a \(\{100\}_\alpha\) habit plane, lies either parallel or perpendicular to the normal \(\{100\}\) cleavage planes and thus presents a more effective barrier, in the second instance, than Type II precipitate with a \(\{112\}_\alpha\) habit plane. Thus the apparent difference between the minimum in yield stress and that in transition temperature as a function of nitrogen concentration may be due to the effect of the precipitates on the propagation of a crack.
SUMMARY

The salient features of the results obtained in this study are:

a) A minimum in transition temperatures, yield strengths, and a maximum in resistance ratios, with no change in hardness values, as a function of nitrogen concentration after aging at temperatures greater than 600°C.

b) The gradual decrease in transition temperatures with increasing nitrogen concentrations for low temperature aging.

c) The progressive increase in resistance ratios while hardness values exhibit a maximum as a function of aging temperatures at temperatures of 455°C and below.

d) The changes in microstructure and fracture surfaces as a function of nitrogen concentration and heat treatment. No simple explanation was found for this variety of behavior; however, a model based on successive stages of precipitation of nitrogen retained in solution upon quenching and changes in precipitate morphology and density has been proposed. In brief, the proposed sequence of events during aging is as follows:

1) The evidence suggests that in the as-quenched state incoherent Type I precipitates are present in all alloys, Type II in alloys of high nitrogen concentrations, a minimum of 8-10 ppm nitrogen is retained in solid solution, and some coherent particles may be present.
2) During aging at low temperatures the supersaturated nitrogen precipitates as additional coherent or semicoherent particles.

3) During overaging at low temperatures these particles dissolve and the nitrogen is absorbed by growth of the pre-existing Type I and II precipitates or the formation of new Type I precipitates.

4) During aging of low nitrogen alloys at high temperatures the supersaturated nitrogen first precipitates as virtually incoherent particles. Subsequent aging causes solution of the particles and precipitation as new Type I particles.

5) During aging of high nitrogen alloys at high temperatures the supersaturated nitrogen precipitates on pre-existing Types I and II precipitates, and as the nitrogen concentration increases, Type II precipitates gradually become predominant and control the behavior of the alloys.

In conclusion, it has been shown that a minimum in the brittle-ductile transition temperature of chromium may be achieved with a nitrogen concentration of about 350 ppm by aging at temperatures over 600°C. A model has been proposed based on the associated changes in mechanical properties and microstructures. It has been established that Cr₂N precipitates during quenching and aging and that it assumes two habit planes, \( \{100\}_\alpha \) at low concentrations and both \( \{112\}_\alpha \)
and \{100\}_\alpha at high concentrations of nitrogen. However, more work is required to establish precisely the effects of these precipitates on the yield and fracture phenomena of chromium.
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APPENDIX

Electron Microscopy

Although electron microscopy was used primarily for the identification of precipitates and determination of their habit planes, a few general observations were noted. The precipitates in many cases appeared similar to the electron micrographs published by Yoshida et al. (26), including the unexplained contrast bands within the precipitates. Most areas were almost free of dislocations, but dislocation tangles around precipitates were not unusual.

Habit Planes of Precipitates

Transmission electron microscopy was employed to determine the habit planes of the two types of precipitates. The apparent direction in which an elongated precipitate lies in a plane of observation (foil plane) is the zone axis common to the foil plane and the matrix plane on which growth of the precipitate actually occurs (habit plane). By comparing the possible habit planes compatible with the zone axes observed on foil planes of several orientations, and assuming a single habit plane was being observed, it was possible to determine the only plane which was common to all the observations. This then was assumed to be the habit plane of the precipitate.

Representative examples of such observations are shown in Table 4 including the type of precipitate to be expected.
Table 4. Habit planes of precipitates from electron microscopy

<table>
<thead>
<tr>
<th>Foil plane</th>
<th>Zone axis</th>
<th>Possible habit planes</th>
<th>Type of precipitate</th>
</tr>
</thead>
<tbody>
<tr>
<td>(103)</td>
<td>&lt;010&gt;</td>
<td>(001) (110)</td>
<td>I</td>
</tr>
<tr>
<td>(110)</td>
<td>&lt;110&gt;</td>
<td>(001) (111)</td>
<td>I</td>
</tr>
<tr>
<td>(001)</td>
<td>&lt;010&gt;</td>
<td>(100) (101)</td>
<td>I and II</td>
</tr>
<tr>
<td>(210)</td>
<td>&lt;002&gt;</td>
<td>(010) (110)</td>
<td>I and II</td>
</tr>
<tr>
<td>(111)</td>
<td>[110]</td>
<td>[100] [111] (110)</td>
<td>I and II</td>
</tr>
<tr>
<td></td>
<td>&lt;123&gt;</td>
<td>(121) (032) (331) (153)</td>
<td></td>
</tr>
<tr>
<td>(001)</td>
<td>&lt;120&gt;</td>
<td>(211) (210) (212) (213)</td>
<td>I and II</td>
</tr>
<tr>
<td></td>
<td>&lt;210&gt;</td>
<td>(121) (120) (122) (123)</td>
<td>I and II</td>
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</tbody>
</table>

from light microscopy. If a single habit plane was responsible for both zone axes on the (103) plane, the only low index plane compatible with both zone axes was of the form {001}. This conclusion was verified by comparison of the results for
the \(1\overline{1}0\) and \(00\overline{1}\) planes as shown in the table and by many other observations. Yoshida et al. (26) also concluded that a nitride formed on the \(\{001\}\) planes. From the similarity in appearance between the electron and light micrographs and comparison with single crystal observations, this habit plane was assigned to the Type I precipitate.

The habit plane of the Type II precipitate was similarly determined to be of the form \(\{1\overline{1}2\}\) from comparison of the \(1\overline{1}1\) and \(001\) planes of observation shown in the table. Figure 29 is an example that shows both types of precipitate. The foil thickness calculated from the apparent width of the Type II precipitate was 1200 \(\AA\), while the same calculation based on the Type I precipitate yielded a value of 1100 \(\AA\) — further confirmation of the assigned habit planes.

The determinations of habit planes by electron microscopy were supported by conventional metallographic observations of precipitates in oriented single crystals. The results with some of the possible habit planes are presented in Table 5. An insufficient number of planes of observation were used to make it possible to assign habit planes based on these observations alone.

**Precipitate Identification**

Precipitates of both types were identified as hexagonal \(\text{Cr}_2\text{N}\) by electron diffraction. An example is shown in Figure 30. These results were verified by extracting the precipi-
Figure 29. Cr-325 ppm N aged at 750°C showing both Types I and II precipitates, X20,000.
Figure 30. Cr-675 ppm N aged at 455°C for 14 hours, Type II precipitate, X26,500
Table 5. Habit planes of precipitates from optical metallography

<table>
<thead>
<tr>
<th>Plane ofobservation</th>
<th>Zone axis</th>
<th>Possible habit planes</th>
<th>Type of precipitate</th>
</tr>
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<tbody>
<tr>
<td>{111}</td>
<td>[110]</td>
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<td>II</td>
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</table>

tates from an alloy nominally containing 660 ppm nitrogen which had been aged for 10 hours at 635°C. The microstructure showed that both types of precipitate were present as well as a considerable amount of precipitate in the grain boundary. Only Cr₂N lines were found in the x-ray diffraction pattern, and consequently it was concluded that not only both forms of precipitate within the matrix, but also the grain boundary precipitate was Cr₂N.