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INDUSTRY PROGRAM OF THE COLLEGE OF ENGINEERING

A STUDY OF THE INFLUENCE OF NITROGEN ON THE CREEP-RUPTURE PROPERTIES OF A NICKEL-CHROMIUM ALLOY HARDENED WITH TITANIUM AND ALUMINUM

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ABSTRACT

The objective of this investigation was to study the effect of nitrogen on the creep-rupture properties of a simplified 78 Ni - 19 Cr - 2 Ti - 1 Al alloy subject to precipitation hardening by the γ' phase, $Ni_3(Al, Ti)$. The study was designed to first determine if nitrogen was beneficial or deleterious to properties, and second, with this established, to study the effects of nitrogen on the structure of the alloy and relate these structural effects to properties.

Heats were prepared in a vacuum induction melting furnace with nitrogen content increasing from 0.003 to 0.034 percent. To minimize the effects of factors other than nitrogen, the content of Mn, Si and C, and other elements in the alloy was kept low, and uniform melting and hot working procedures were used for producing the materials. The influence of nitrogen on the creep-rupture properties was evaluated by tests at 1350°F and 28,000 psi. Structural studies were carried out on samples from interrupted and completed creep-rupture tests as well as on samples after heat treatment, using optical and electron microscopy, x-ray diffraction and mechanical property measurements.

Nitrogen has a pronounced strengthening effect on the alloy at high temperatures. Raising the nitrogen from 0.003 to 0.013 percent effectively increased creep resistance. At the same time, nitrogen up to 0.034 percent increased the resistance to fracture by delaying the initiation of and increasing the time and deformation in tertiary creep. The increased resistance to creep and fracture resulted in increased rupture life with the most marked effect found from increasing the nitrogen from 0.003 percent (average rupture life 100 hours) to 0.013 percent (average rupture life 500 hours).

Several structural effects indicate that the increased creep

resistance was related to the increase of nitrogen in solution prior to creep-rupture testing. The alloy fractured during creep-rupture tests by the formation and growth of micro-cracks in the grain boundaries. The formation of micro-cracks occurred at the interface between the matrix and carbide-type particles in the grain boundaries. The delay in the initiation of tertiary creep was related to the increased time required for the appearance of micro-cracks. The reduction of the rate of tertiary creep and the increase in the duration of tertiary creep was related to the reduction in the number of micro-cracks growing during this period of creep. Thus, the increased rupture life was due to a reduction in the susceptibility to micro-cracking. This, in turn, was associated with a change in the type of precipitation in the grain boundaries. In the low nitrogen heat the predominant type of carbide was $Cr_{23}C_6$, and in the higher nitrogen heats the predominant carbide was Cr_7C_3.

Some possible causes for the influence of nitrogen on the creep-rupture properties were discussed. It was hypothesized that the segregation of nitrogen atoms in dislocations was stabilized by its tendency to form nitrides of titanium or aluminum. These "atmospheres" were effective for increased creep resistance prior to the appearance of identifiable nitride precipitates. It seems probable that nitrogen decreased the solubility of carbon in the matrix or substituted into the intergranular compounds or both, thereby promoting the formation of more Cr_7C_3 rather than $Cr_{23}C_6$ precipitates. It is generally recognized that cracking during creep in alloys of the type studied is reduced when Cr_7C_3 is formed rather than $Cr_{23}C_6$. Although the cause has not been established, it appears as if there is an increase

in boundary forces between the Cr_7C_3 particles and the matrix.

In view of the way nitrogen operated in the experimental alloy, it was clear that its effects could vary if the mechanism of creep was changed by altering testing conditions or if phase relationships were altered by changes in composition or heat treatment.

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INTRODUCTION

Although nitrogen is always present in alloys melted in air, in most cases its effects on creep-rupture properties and micro-structure are not well established. However, in recent years its value as a hot strengthener has been shown for a few steels. It is purposely added to many alloys of the non-precipitation hardening type to improve properties and in a few cases it has been shown to contribute to creep-rupture strength through reactions similar to strain aging or by precipitation of nitrides. In other cases it has been shown to influence creep-rupture properties by such controls of structure as the stabilization of the face-centered cubic structure in stainless steels. The influence of nitrogen on the high temperature properties of alloys other than steel is not clear and in fact it appears that its effect may even be deleterious, since aluminum and titanium bearing nickel-base alloys were reported to have improved properties when melted in vacuum. *

Vacuum melting could be expected to reduce nitrogen to very low amounts in such alloys and consequently its removal could be one of the reasons for improved properties. On the other hand, the increased high temperature properties attributable to vacuum melting could result from other effects, such as reduction of oxygen content and volatilization of trace amounts of elements such as lead and antimony which are known to be harmful to properties at high temperatures[2]. Furthermore, pronounced improvements in high temperature properties have been derived from boron and zirconium introduced into the metal through reaction with crucible ceramics during vacuum melting[3,4].

* The superscripts refer to literature listed under REFERENCES.

Consequently, the question of whether the removal of nitrogen during vacuum melting of nickel-base alloys increased the high temperature properties is complicated by the other effects mentioned. In fact, it is entirely possible that the removal of nitrogen decreases creep-rupture properties but is masked by the pronounced improvements derived from secondary effects.

The primary objective of this investigation was to study the effects of nitrogen on creep-rupture properties of a simplified nickel-chromium alloy subject to hardening by the precipitation of $Ni_3(Al, Ti)$. The study was designed to first determine if nitrogen was beneficial or harmful to creep-rupture properties and then to study the structural effects of nitrogen hoping to be able to relate these effects to the properties. It was hypothesized that nitrogen would be expected to act in two ways: as an interstitual solid solution element it could increase creep resistance; secondly, as an element which affect phase transformations it could be either beneficial or detrimental.

Since the objective was to study the effect of nitrogen in as simple a nickel-base alloy as possible, subject to the occurrence of γ' precipitation, a 78 Ni - 19 Cr - 2 Ti - 1 Al alloy was chosen. The content of Mn, Si and C, as well as other elements, was kept low, and the experimental heats were prepared under conditions designed to minimize all factors except the role of nitrogen.

REVIEW OF LITERATURE

It was anticipated that the effect of nitrogen on creep-rupture properties might be through its influence on the matrix properties or phase relationships. Consequently, the literature has been reviewed with this in mind.

Effects of Nitrogen on Creep-Rupture Properties

A search of the literature revealed that very little research has been conducted on the influence of nitrogen on high-temperature properties. No direct literature was found relating creep-rupture properties of nickel-base alloys to nitrogen. However, the fact that vacuum melting of many of these alloys resulted in improved properties[1] suggested that nitrogen might have a deleterious effect. Yet, in other alloys, especially steels, nitrogen has been purposely added to improve properties. Hum and Grant[5] and subsequently Monkman, Price and Grant[6] found that nitrogen increased the creep-rupture properties of 18-8 stainless steel. They suggested that nitrogen increased the creep-rupture properties by two means. First, nitrogen increased strength by solid solution strengthening of the austenite matrix, and second, nitrogen in solution suppressed the formation of sigma and ferrite by stabilizing the austenite matrix. However, this strengthening effect was time and temperature dependent since nitrides precipitated during creep exposure. Zackay, Carlson and Jackson[7] found that nitrogen increased creep-rupture properties of Cr-Mn steels. Bardgett and Gemmill[8] have shown a relation between creep strength and aluminum present as aluminum nitride in some carbon steels. Dickinson[9] studied the effect of deoxidation on the creep characteristics of plain carbon steel and found creep resistance to be related

directly to dissolved nitrogen. He proposed a modification of Cottrell's strain aging mechanism to explain this behavior. Dumbleton[10] made some creep experiments on single crystals of zinc treated in nitrogen to develop yield points and a capacity for strain aging. Creep curves obtained at 195°F under a stress provided by a soft spring showed a remarkable decrease in creep rate due to strain aging.

Microconstituents in Titanium and Aluminum Hardened Nickel-Base Alloys

Taylor and Floyd[11, 12, 13] have published the results of investigations of the nickel-rich corner of the nickel-chromium-titanium, the nickel-chromium-aluminum and the nickel-titanium-aluminum systems. Recently, Taylor[14] published the results of a study of nickel-rich quaternary alloys of the nickel-chromium-titanium-aluminum system. In the binary nickel-titanium system the hexagonal Ni_3Ti phase exists in equilibrium with the nickel-rich solid solution. Replacing nickel by chromium reduces the solubility for titanium. According to Taylor and Floyd, Ni_3Ti takes practically no nickel, chromium or aluminum into solution.

In the nickel-aluminum system the cubic Ni_3Al phase (γ'), having the ordered Cu_3Au-type structure, exists in equilibrium with the nickel-rich solid solution. Substitution of chromium for nickel reduces the solubility for aluminum. In the binary nickel-aluminum system the γ' phase has a slightly larger lattice parameter than the matrix. Chromium dissolves in the matrix and the γ' phase and increases the lattice parameter of both phases.

In the ternary nickel-titanium-aluminum system the two phases Ni_3Ti and Ni_3Al exist in equilibrium with the nickel-rich solid solution. In contrast to Ni_3Ti, Ni_3Al was observed to have a considerable range of homogeneity. Taylor and Floyd found that up to three out of every five aluminum atoms could be replaced by titanium.

Hignett[15] mentioned that the hardening of Nimonic 80 (75 Ni - 20 Cr - 2.1 Ti - 1.1 Al - .05 C) was due to the controlled precipitation of $Ni_3(Ti,Al)$ having the cubic Ni_3Al structure. Nordheim and Grant[16] in an extensive study of alloys based on the 80-percent nickel 20-percent chromium composition with additions of titanium and aluminum confirmed the statement of Hignett.

Baillie and Poulignier[17] studied the precipitation of γ' in 80-20 type Ni-Cr alloys with the aid of the electron microscope. They found that the average particle diameter varied as an exponential function of temperature while the number of particles per unit area varied linearly with temperature in the range of 1300° to 1500°F.

Several other microconstituents have been identified in Nimonic type alloys. These include $M_{23}C_6$[18,19,20,22], Cr_7C_3[21,22], TiC[18,20,22], TiN[22,23] and Ti(CN)[23]. The occurrence of these phases is dependent on alloy composition, melting conditions and thermal history. According to Beattie and VerSnyder[23] TiN and Ti(CN) form in the melt prior to solidification.

Relation of Microconstituents in Titanium and Aluminum Hardened Nickel-Base Alloys to Creep-Rupture Properties

It has been shown that the hardening of Nimonic type alloys is due to the controlled precipitation of $Ni_3(Ti, Al)$ (γ')[15, 16, 17]. It is also widely held that the favorable high temperature properties of these alloys results from the same precipitation[24]. However, attempts to relate high temperature properties to the amount of γ' have not been completely successful.

Pfeil, Allen and Conway[25] reported that an 80-percent nickel - 20-percent chromium alloy containing 0.20 - 0.30 percent aluminum exhibited the highest creep strength for titanium contents between 1.65 and 2.75 percent. Poulignier and Jacquet[26] observed that by keeping the sum of the atomic percentage of titanium and aluminum constant (equal to about 5.2) but increasing the titanium to aluminum atomic ratio from 0.8 to 1.3, the minimum creep rate at 1382°F and 17,800 psi was reduced by a factor of four. Presumably, the increased creep strength of these alloys can be related to the amount of γ' precipitated or its mode of precipitation as affected by changes in titanium and aluminum content. Frey, Freeman and White[27], and Brockway and Bigelow[18] found that the dispersion of γ' particles prior to creep exposure in an Inconel-X alloy correlated with creep-rupture properties at 1200°F, a temperature which was low in the aging range for this alloy. They did not observe this correlation with rupture tests at 1500°F, which was high in the aging range for the alloy.

Betteridge and Smith[28] suggested from comparative tests on three heats of Nimonic 90 (55.5 Ni - 19.5 Cr - 19.5 Co - 2.5 Ti - 1.2 Al - .08C) that the highest stress-rupture properties were obtained

with the greatest content of precipitated phases. However, some of the marked effects of heat treatment on creep-rupture properties could not be related to changes in γ' precipitation. On the other hand, work on Nimonic 80A by the same authors showed that there was no inflection in the rupture stress-temperature relation on crossing the temperature at which the structure changed from that of matrix containing a dispersed γ' phase to that of a complete-solid solution. It would appear then, that in this alloy the presence of the precipitated phase has no important effect on the rupture stress. These authors suggest that, "It is possible that these differing conclusions (between Nimonic 90 and 80A) can be reconciled by assuming that the increase in stress-rupture strength due to the formation of a precipitated phase is, in these particular alloys, sufficient only to compensate for the decrease in strength due to the loss of the precipitated material from solid solution." Baillie[29] observed that, in several alloys examined, the best creep resistance was found in those having the highest surface density of precipitated phase (as seen in electron micrographs) prior to creep exposure. Bettridge and Franklin[21] found that variation in the temperature of precipitation of the γ' phase affects to a small degree both the creep rate and the extension at which fracture occurs. However, the effect of the γ' precipitate could not be isolated unequivocally since more γ' precipitated during creep exposure and carbides precipitated both during the aging treatment and the creep exposure.

Further work has been done in attempts to relate microstructural changes other than γ' precipitation to creep and rupture properties. Betteridge and Smith[28] were able to correlate some marked effects of heat treatment with a grain boundary precipitation of carbide. Betteridge and Franklin[21] were successful in relating the distribution of the

Cr_7C_3 grain boundary carbide to rupture life in Nimonic 80A alloys. They found that the best rupture life correlated with an optimum distribution of Cr_7C_3 in the boundaries.

Although much work has been done on the effect of microstructure on creep strength, only a small amount of work has been done on the effect of creep exposure on microstructural changes in these alloys. Baillie and Poulignier[17] did not find an effect of creep deformation on the γ' precipitation, but they did note an agglomeration at grain boundaries during creep. Mathieu[30] also observed in Nimonic 80 and Nimonic 90 alloy turbine blades removed from service agglomeration at the grain boundaries. He suggested that these agglomerations were chromium carbides or nitrides and in the case of alloys high in titanium and aluminum, γ'. The main significance attached to this agglomeration was that it led to a considerable decrease of chromium in regions adjacent to the boundary.

EXPERIMENTAL PROCEDURES

An alloy with a nominal composition of 78 Ni - 19 Cr - 2 Ti - 1 Al was prepared with increasing amounts of nitrogen. The content of Mn, Si and C, as well as other elements, was kept low. The general procedure was to investigate the effect of these nitrogen additions on creep-rupture properties; and then, in order to develop an understanding of the effect of nitrogen on the properties, the influence of thermal treatment and stress on the microstructural, hardness, and lattice parameter changes of the alloys were studied as a function of nitrogen content. The experimental methods are described in detail in the following sections.

Materials

The alloys were prepared as 10-pound melts in The University of Michigan vacuum induction melting furnace using electrolytic nickel, "Shieldalloy" chromium, 99.99 percent pure aluminum pig, commercially pure titanium, spectrographic grade carbon, and chromium nitride, analyses of which are given in Table I.

A uniform melting procedure was used for all the heats. The nickel, chromium and carbon (added for deoxidation) were melted in an alumina (Tycor) crucible. During the initial melt-down the maximum pressure did not exceed 25 microns and the minimum pressure varied from 1 to 5 microns with a leak rate of 6 microns per minute. After the nickel and chromium melted and the carbon-oxygen reaction was completed, the titanium and aluminum were added and allowed to melt into the nickel-chromium-carbon base.

The last addition was chromium nitride for those heats in which it was desired to increase the nitrogen content. First attempts to add

nitrogen in this manner resulted in a violent reaction immediately after the chromium nitride was added to the melt. This reaction blew most of the chromium nitride from the liquid surface thereby causing a very low nitrogen recovery. This problem was circumvented by adding argon gas to a pressure of 400 mm just prior to the chromium nitride addition. Under these conditions chromium nitride entered the melt in a quiet manner. After the chromium nitride addition the temperature of the melt was adjusted to 2800°F, and the melt was then poured slowly into a 2-1/2 inch - diameter copper mold. The argon addition was made to all heats even though chromium nitride was not added. Total time from start of melting to pouring varied between 68 and 75 minutes for all the experimental heats. The heats were numbered to indicate the relative amount of nitrogen in the order: 1(0.003-percent nitrogen), 2(0.013-percent nitrogen), 3(0.027-percent nitrogen), and 4(0.034-percent nitrogen). Since nitrogen was not added to Heat 1 this heat represents the lowest nitrogen content attainable with the melting stock and melting technique used.

The 10-pound ingots were processed as follows:

1. Heated 6 hours at 2150°F to promote homogeneity of the ingot. Air cooled.
2. Surface defects removed by grinding.
3. Rolled at 1950°F to 1.1-inch square bar stock using 19 passes with a 10-minute reheat between each pass. Reduction per pass was about 0.1-inch.
4. Reheated to 1950°F for 15 minutes after last reduction. Air cooled.

Chemical analyses were made on sections of the bar stock which were originally at the ingot center. Nitrogen analyses were determined

by the Kjeldahl technique and oxygen analyses by the vacuum fusion technique. The results are listed in Table II.

Creep-Rupture Testing

The testing program was initiated to determine if nitrogen affected creep-rupture properties and to obtain a quantitative measure of the extent of this effect. For this study specimens were solution treated at 2000°F and aged 24 hours at 1400°F prior to testing at 1350°F. The majority of the tests were run at 28,000 psi stress. However, for a few tests on the 0.003-percent nitrogen heat the stress was lowered to 24,000 psi.

To evaluate the influence of γ' density or dispersion on the creep-rupture properties at the same nitrogen levels, specimens were solution treated at 2000°F and aged 24 hours at 1350°F or 1450°F prior to testing. Tests were made on specimens solution treated at 1700°F and aged 24 hours at 1400°F to determine the effects of prior history on the high temperature properties.

Creep-rupture testing was performed in stress-rupture units with strain measurements being made with an extensometer-mirror system with a sensitivity of 0.000005 inch per inch.

The original 1.1-inch-square bar stock was cut into 3-1/2-inch lengths and then sectioned lengthwise into 4 bars each about 1/2-inch square. These bars were heat treated to the required condition and machined to 0.250-inch diameter specimens with a 1-inch gage length. The specimens were loaded in the stress-rupture units and brought to temperature without stress. Since the time to reach the correct temperature distribution varied between 2 and 4 hours, a uniform heat-

ing time of 4 hours was used before the stress was applied.

Most of the specimens were tested to complete failure. In a few cases the tests were interrupted at a preselected deformation to determine the effect of creep on the microstructure. In these cases the stress was released and the specimen removed from the furnace.

High Temperature Tensile Tests

Cottrell[31] and Lubahn[32] have pointed out that in a stress-strain curve the occurrence of strain aging during deformation is usually shown by a series of steps (serrations) which indicate that either the stress, the rate of strain, or both, alternate repeatedly between two values.

To examine the strain aging characteristics of these experimental heats, as influenced by nitrogen content, specimens solution treated at 2000°F and aged 24 hours at 1400°F were subjected to tensile tests at 900°F using a crosshead travel rate of 0.08 inches per minute. Strain was measured by an extensometer system employing a microformer type strain gage as a sensing element. The signal from the microformer strain gage was fed to an automatic recording device which simultaneously received a load signal. The load versus strain curve was automatically recorded on a rotating drum. However, once the contact points of the microformer were separated by a large increase in strain the microformer could not drive fast enough to close the contact points before the next jump occurred. Under these circumstances the drum rotates (rotation of the drum was a measure of strain) at a constant rate so that later in the test the recording device plotted load versus time rather than strain.

Thus, the curves obtained from these tests are initially a measure of load versus strain and in the later stages load versus time.

Thermal Treatments

Several thermal treatments were used to investigate the influence of nitrogen on microstructure. These treatments and the reasons for them are listed below:

1. Specimens were heated to temperatures between 1350°F and 2000°F, held for various lengths of time depending on the temperature and water quenched. These heat treatments were designed to produce information on the type of phases present and the temperatures at which they went into solution in the matrix.
2. Samples were heated to 2000°F (where complete solution of the active phases occurred) held 4 hours and water quenched. They were then reheated to 1350°F, 1400°F or 1450°F for 1/4, 1, 6, 24, 100, 250, 500, and 1000 hours. The precipitation that occurred in this temperature range was readily followed by election and optical microscopy.

Hardness

Using one hardness tester, Rockwell B hardness measurements were taken on all samples. Five impressions were made and the average value reported. In the range of about 80 to 103 Rockwell B a difference of average values of 1 Rockwell B was found significant because of the extremely small range in hardness values obtained from the five measurements. However, between 65 and about 80 Rockwell B a differ-

ence in average value of 2 Rockwell B was necessary before a difference in hardness could be considered significant. This resulted from an increase in the range or spread of hardness values from the five readings.

Lattice Parameter

Lattice parameters of the matrix were determined on solid samples using the Geiger-counter x-ray spectrometer in conjunction with the rotating flat specimen holder. The scanning speed, slit widths and time constant were chosen following the suggestions of Klug and Alexander[33] and the Norelco instruction manual for the spectrometer unit. These conditions were adhered to as rigidly as possible. However, for extremely weak lines (420, α_1, α_2 of samples aged 1000 hours) the time constant was increased in order to obtain a measurable diffraction peak. Klug and Alexander[33] point out that a change in the time constant may introduce a line shift on the recorder chart and hence introduce an error in the lattice parameter value. Hence, when these data were extrapolated to obtain the a_o lattice parameter value less weight was placed on diffraction peaks determined in this manner.

Each diffraction profile was traced over twice at a scanning speed of 1/4° 2θ per minute. The 2θ value was determined as the average peak value from these traces. For the majority of the lattice parameters determined the 2θ values of the 420 α_1, α_2, 331 α_1, α_2 and the 311 α_1 diffraction lines were determined using copper radiation (λ Cu-K_{α_1} = 1.5405 Å[34]). The 311 α_2 diffraction line was examined when it was sufficiently well resolved from the α_1. The 222 α_1 diffraction line was used when one or more of the high angle reflections were poor. The θ values of these lines covered the range of 45 to 76°. The

extrapolation technique of Taylor and Sinclair[35] and Nelson and Riley[36] was used to determine the values of a_o. The lattice parameters were not corrected for variations in room temperature. However, room temperature varied from about 75° to 80°F during the study of lattice parameters and such a variation would lead to a maximum effect of temperature on the a_o value of 0.0002Å.

The reported lattice parameters are in the majority of cases single determinations from one sample. However, several samples were examined for reproducibility of the lattice parameter value. It was found that the reproducibility depended considerably on the intensity of the lines examined and these in turn depended markedly on thermal treatment. This variation of diffraction line intensity with thermal treatment in these alloys has been observed by others[37]. In samples from which fairly sharp intense diffraction lines were obtained the reproducibility of the lattice parameter was within the limits of ±0.0004Å. On the other hand, if more than one of the high angle lines were poor it was very difficult to obtain reliable 2θ values and the limits of reproducibility were not better than ±0.0004 nor worse than ±0.0006Å. Variations in lattice parameter values for duplicate samples were determined for a few conditions of thermal treatment. It appeared from these tests that the reproducibility of the lattice parameter was about the same as mentioned above.

Metallography

Light Microscopy

Metallographic specimens were mechanically polished on 120-, 240- and 600-mesh silicon carbide papers in that order. The final

mechanical polish was performed on wet cloth with Linde A powder. In a few cases the specimens were examined in this condition to investigate the form, color and distribution of Ti(CN) particles. However, in the majority of cases the samples were then electrolytically polished in a solution of 10 parts of perchloric acid (70 percent) and 90 parts of glacial acetic acid. To obtain a satisfactory polish the solution was cooled to about 50°F. A current density of 10 amperes per square inch for a period of 15 seconds usually gave good results.

The method of Bigelow, Amy and Brockway[38] was used to delineate the precipitating phases. Electrolylitic etching for 5 to 15 seconds at a current density of 0.5 amperes per square inch in a solution of 12 parts of phosphoric acid (85 percent), 45 parts of sulfuric acid (96 percent) and 41 parts of nitric acid (70 percent) usually gave adequate results for optical observations.

Electron Miscroscopy

The preparation of specimens for electron microscopy was identical to that used for optical microscopy. Electrolytic etching was performed in the same etching solution, but was carried out at a current density of about 0.3 to 0.4 amperes per square inch for 3 to 7 seconds.

Replication of the prepared surface was accomplished using a collodion-amyl acetate solution. Polystyrene latex spheres were placed on the collodion replica to provide an internal standard for magnification and to indicate the direction of shadowing. The collodion replicas were then shadowed with palladium to increase contrast and reveal surface contours. In this connection it should be noted that particles with shadows in the same direction as those from the polystyrene latex spheres indicate a depression on the original metal

surface. Conversely, particles with shadows opposite to those cast by the spheres are protrusions above the original metal surface.

The micrographs shown are contact prints from the original plates causing the polystyrene spheres to appear black and "shadows" white.

Quantitative Microstructure Measurements

In order to study quantitatively the changes in microstructure due to thermal treatments and creep, techniques were developed to obtain information on the amount of γ' precipitated and micro-cracks formed.

A quantitative measure of γ' was obtained in terms of the surface density of particles as measured directly from electron micrographs at 18,000X. The number of particles in three different 1 square inch areas were counted and the average value reported. Usually this survey involved two separate micrographs from different areas of the same sample.

It was evident that a measure of γ' particle size would be helpful in evaluating differences in aging characteristics. To obtain a reasonable measure of particle size, the electron micrographs were enlarged to 54,000X. The size of about 25 particles chosen at random on the enlargement was measured and the average value recorded. It was recognized that a more refined technique might yield better values. Baillie and Poulignier[7] did use such a technique but found that the average particle size did not differ significantly from the size of the γ' particles as measured on the electron micrographs. The average distance between γ' particle in a plane surface (dispersion) was calculated from the average number per unit area and average size of these

particles.

Electrolytically polished and etched surfaces were examined at 1000X to detect micro-cracks. Micro-cracks were counted in a 0.010 square inch area in the central portion of the creep specimens. It was difficult to differentiate between micro-cracks and precipitates when the size of the micro-crack was less than 1 micron. Therefore, for this comparison only micro-cracks 1 micron or larger were counted.

During the study of micro-crack formation and growth it became evident that both the number of micro-cracks and their size were important. Therefore, the lengths of 100 to 150 micro-cracks were measured and the average value recorded. The product of the number of micro-cracks per unit area and the average length of these micro-cracks gave a measure of average length of crack present per unit area. The product of number of micro-cracks and average size is referred to as the "extent of micro-cracking."

Electron Diffraction

The extraction replica technique of Fisher[39] was used in an attempt to identify phases in these alloys by electron diffraction measurements.

For extraction of grain boundary phases the microfractographic techniques of Plateau, Henry, and Crussard[40] were employed. The sample was fractured at low temperatures to produce an intercrystalline fracture. Carbon replica films were deposited on the fractured surface by the method of Bradley[41] and backed by a supporting film of collodion. These samples were electrolytically etched in a solution of 2 parts phosphoric acid (85 percent) to 8 parts of water until the replica separ-

ated from them. The replicas were washed with distilled water, placed on nickel screens, washed again, and the collodion was then removed from the carbon film with amyl acetate by the method of Jaffe as described by Fullam[42].

These replicas were shadowed with aluminum to provide an internal standard for measurement of "d" values. Electron micrographs and selected area diffraction photographs were obtained on an RCA Model EML electron microscope.

X-Ray Diffraction

The main method used to identify precipitated particles was x-ray diffraction techniques on residues from bromine-anhydrous methyl alcohol. Samples were also exposed to a solution of 10 parts hydrochloric acid (sp. gr. 1.19) - 90 parts water for 2 hours at a current density of 0.5 amperes per square inch.

After the extractions were completed the solutions plus the residue of separated particles were centrifuged and the solution decanted from the residues. The residues were washed with anhydrous methyl alcohol and re-centrifuged. The last step was repeated several times until the remaining alcohol solution was completely clear.

Normally, carbides and Ti(CN) are either unattacked or attacked very slowly in the bromine extraction while the nickel-base matrix and γ' phase are dissolved rapidly. The results of the electrolytic extraction in hydrochloric acid are similar. The electrolytic hydrochloric acid separation technique was used for two reasons; first as a check against the separation in the bromine solution and second, because Ti(CN) is attacked by this solution. It was hoped that Ti(CN) would be

completely dissolved thereby eleminating it from the residues.

Hull-Debye-Scherrer X-ray diffraction patterns were obtained from a 114.6mm diameter camera using copper K_α radiation (λ Cu-K_{α_1} = 1.5405Å[34]). A thin nickel foil, (0.001-inch) was placed in front of the film to filter the fluorescent radiation produced from the sample. Under these conditions an exposure of 12 hours was found to be satisfactory. The "d" values were determined from the charts of Parrish and Irwin[43].

The intensity of the diffraction lines are visual classifications and are self-consistent within a particular film. An arbitrary intensity code was chosen to indicate relative intensities of the lines in the diffraction films. A scale of 1 through 8 indicates a change in intensities from weak to strong. This scale corresponds roughly to the usual classification of "very very weak (VVW)" to "very strong (VS)." However, as many of the diffraction lines were extremely weak and not amenable to the usual classification a scale of negative numbers, -1 to -3, was selected to indicate the extremely low intensity of these lines. Since such a classification could be biased by the observer, a microphotometer check was made on these intensities whenever the quality of the film permitted.

The microphotometer traces were obtained on the Leeds-Northrup recording microphotometer. The integrated intensity (area under the curve) and the width at half height were measured. The agreement between the visual and microphotometer methods for relative intensities was excellent for those films that could be checked.

Unfortunately, the microphotometer could not be used satisfactorily on the few films with dense backgrounds. Furthermore, visual examination was necessary for the extremely weak lines because the microphotometer did not differentiate such lines from the background.

EXPERIMENTAL RESULTS AND DISCUSSION

The Influence of Nitrogen on Creep-Rupture Properties

Nitrogen had a pronounced strengthening effect on high temperature properties at 1350°F. A limited amount of nitrogen effectively increased creep resistance. At the same time, nitrogen, up to the largest amount studied, increased the resistance to fracture by delaying the initiation of and increasing the time and deformation in tertiary creep. The increased resistance to creep and fracture resulted in increased rupture life with the most marked effect found with the first nitrogen addition.

Creep Resistance

As shown in Figure 1, the minimum secondary creep rate was reduced from an average value of 1.5×10^{-5} in/in/hour at 0.003-percent nitrogen to 0.44×10^{-5} in/in/hour at 0.013-percent nitrogen. Increasing nitrogen to 0.027 and 0.034 percent did not cause a further change in minimum secondary creep rate. Aging at 1350°F, 1400°F or 1450°F prior to testing had little influence on creep resistance at all nitrogen levels. The creep rate of specimens aged at 1350°F or 1450°F (after solution treatment at 2000°F) prior to testing (Table III, Figure 1) fell close to the range obtained from duplicate tests on specimens aged at 1400°F. The creep resistance of specimens solution treated at 1700°F prior to aging at 1400°F was similar to that obtained from specimens solution treated at 2000°F prior to aging (Table III).

Tertiary Creep

Figures 2 and 3 relate the initiation and duration of tertiary creep to nitrogen content. The average time for the initiation of tertiary creep increased from 50 hours at 0.003-percent nitrogen to 293 hours at 0.013-percent nitrogen. Increasing the nitrogen to 0.034-percent caused a

further but smaller delay in the initiation of tertiary creep. Although additions of nitrogen above 0.013-percent had a small effect on the initiation of tertiary creep, these additions caused a marked increase in the duration of tertiary creep. The length of time in tertiary creep increased from 50 hours at 0.003-percent nitrogen to 430 hours at 0.034-percent nitrogen.

As shown in Figure 4, nitrogen also increased deformation in tertiary creep. It should be pointed out that the last points on these creep curves were obtained from creep data taken just prior to fracture and varied depending on the relation of the time of the measurement to the time when fracture occurred. However, all creep curves for the higher nitrogen heats showed increased deformation before fracture and indicated that nitrogen did cause the deformation in tertiary creep to increase slightly before fracture.

Rupture Life

Average rupture life at 1350°F and 28,000 psi stress increased from 100 hours at 0.003-percent nitrogen to 775 hours at 0.034-percent nitrogen as shown by Figure 5. The increase of nitrogen from 0.003-percent to 0.013-percent caused the most pronounced increase in rupture life. Further additions of nitrogen to 0.034-percent resulted in a further but proportionately smaller increase in rupture life. As in the case of the minimum secondary creep rate, the influence of nitrogen on rupture life appeared to be relatively independent of aging at 1350°F or 1450°F (Table III, Figure 5). The rupture life of specimens solution treated at 1700°F prior to aging at 1400°F (Table III) was erratic. For the 0.013- and 0.034-percent nitrogen heats the time to rupture was similar to that obtained when the samples were solution treated

at 2000°F. For the other heats the time to rupture was shorter. It appears that the erratic results are due to the effect of prior history, since the solution temperature of 1700°F was lower than the rolling temperature and resulted in incomplete solution of precipitated phases.

It is evident that the first addition of nitrogen increased rupture life by increasing the creep resistance in second stage creep as well as delaying the initiation of and increasing the deformation in tertiary creep. Further nitrogen additions continued to increase the creep resistance in tertiary creep as well as increase the deformation. This caused a further increase of rupture life.

On the basis of the reduction of area and elongation values (Table III), it seemed that nitrogen had little or no effect on ductility in the rupture tests. The creep curves, however, did indicate a slight increase in ductility as evidenced by the increased amount of tertiary creep. This was less than one percent, an amount which would not be evidenced in reduction of area and elongation measurements on specimens with a ductility generally less than 3 percent. The error in such measurements masked the small but effective (in terms of increased rupture time) increase in ductility from increased nitrogen.

Relation of Structural Effects of Nitrogen to Creep-Rupture Properties

Existing theories of alloying and structural relations to creep-rupture properties permit certain hypotheses to be made concerning the role of nitrogen in altering creep-rupture properties. These possibilities were accordingly examined. While the results are subject to more than one interpretation, the preponderance of the evidence

indicates that there were two major effects:

1. The increased creep resistance apparently was associated with increased nitrogen in solution in the alloy at the start of creep-rupture tests.
2. The increased resistance to tertiary creep and fracture was due to a reduction in susceptibility to micro-cracking. Apparently, this resulted from a change in the predominant precipitate which formed in the grain boundaries prior to and during creep-rupture testing from $Cr_{23}C_6$ - to Cr_7C_3 - type compounds.

Nitrogen in Solution

Existing theories on the interaction of solute atoms and dislocations and the effects of solute atoms on the lattice constants suggested that the existance of nitrogen in solution should be evidenced by strain aging and expansion of the lattice.

Strain aging-type reactions were found in all the experimental heats and the capacity for strain aging was increased with increased nitrogen. A very small response to strain aging occurred in the 0.003-percent nitrogen heat (Table IV, Figure 6). Increasing nitrogen to 0.013-percent caused a marked increase in strain aging and the capacity for strain aging was further enhanced by the addition of nitrogen to 0.027-percent. No further increase was observed when the nitrogen content was increased to 0.034-percent.

The presence of strain aging-type reactions was not totally unexpected, since Wache[44] found them to occur in air-melted 80 nickel-20 chromium alloys with and without titanium, aluminum and carbon (nitrogen level was not reported). Although Wache did not determine

the cause of the strain aging in these alloys, it appears from the present work that it was probably associated with nitrogen in solution derived from the air.

In order to investigate further the possibility of nitrogen being in solution, the lattice parameters of samples solution treated at 2000°F were determined. The lattice parameter of the matrix increased from 3.5623Å at 0.003-percent nitrogen to 3.5658Å at 0.034-percent nitrogen. Because this increase in lattice parameter could not be accounted for on the basis of other compositional changes (as discussed later) it is considered supporting evidence that nitrogen in solid solution expanded the lattice.

The increased hardness of the solution treated samples with increased nitrogen (Figure 7) seemed to be further evidence of nitrogen in solution although this interpretation of the hardness values may be questionable.

Further evidence that nitrogen in solution increased creep resistance was obtained when specimens of the 0.013- and 0.034-percent nitrogen heats were given a heat treatment designed to reduce the amount of nitrogen in solution prior to creep-rupture testing. The effects of this heat treatment on microstructural changes are discussed in detail later (see section on the influence of intragranular precipitation on creep resistance) but briefly stated, a 1000-hour aging treatment at 1450°F caused the precipitation of a stable compound which appeared to contain nitrogen. This conclusion was supported by the lattice parameter data. A subsequent heat treatment at 1450°F performed to establish the same γ' precipitation that occurred with the usual heat treatment prior to testing did not disturb this stable precipitate. The minimum secondary creep rates of these specimens

(Table XI) were much higher than those found for samples solution treated at 2000°F and aged at 1450°F in which the nitrogen was allowed to remain in solution prior to testing (Table III, Figure 1). Consequently, this is considered further evidence that nitrogen in solution prior to testing increased creep resistance.

The influence of nitrogen in solution on creep resistance in second-stage creep should be considered further. The increase of nitrogen from 0.003-percent to 0.013-percent resulted in a marked increase in creep resistance and at the same time, a marked increase in strain aging. Further consideration of these data show that, although nitrogen above 0.013-percent increased both the strain aging and lattice parameter, the creep resistance was not increased. It appears that only a limited amount of nitrogen effectively increased creep resistance. Dickinson[9] also found that the creep resistance of steels was increased by nitrogen up to a limit beyond which no further change in creep resistance occurred.

According to Cottrell , materials which can undergo strain aging during plastic flow should show improved creep resistance under conditions for which solute atoms can form "atmospheres"[31] or "precipitates in dislocations"[45] which impede or prevent further movements of dislocations. It is possible then, that the creep resistance of this alloy was increased by nitrogen in this manner; however, the reason for the limited effect of nitrogen is not clear. The quantitative relationship between strain aging as measured from tensile tests at a low temperature and the creep resistance at a somewhat higher temperature has not been established and consequently limits the scope of this analysis.

Although, both the strain aging and lattice parameter data indicated that the amount of nitrogen in solution was increased with increased analyzed nitrogen, it must be recognized that the nitrogen contents reported are from Kjeldahl analyses and thus, a great deal of the analyzed nitrogen was obtained from the stable Ti(CN) present in the heats. The amount of these particles increased with increased nitrogen, as shown in Figure 8. As a consequence, the relationship between the amount of nitrogen in solution and the analyzed nitrogen content, as determined by the Kjeldahl technique, is not known. However, it is clear that if it were possible to remove the Ti(CN) and analyze for nitrogen in solution, the influence of nitrogen on mechanical and physical properties would be associated with smaller amounts of nitrogen than were reported.

Micro-Cracking

Since the resistance to tertiary creep and fracture was increased by nitrogen, it appeared that a study of the mode of fracture in these heats would further establish the role of nitrogen on creep-rupture properties.

During creep micro-cracks developed in grain boundaries transverse or nearly transverse to the applied stress with no preference being shown for triple points. The cracks appeared as dark voids in the polished and etched samples and as dark fins with relatively large white shadows in the electron micrographs (Figure 9). Not all transverse grain boundaries showed evidence of micro-cracks. Part of the boundaries were free from micro-cracks while others contained several. As shown in Figure 9, these micro-cracks usually occurred at the interface between intergranular precipitates and the matrix. The initiation,

growth and linking together of the micro-cracks during creep exposure constituted the mode of failure in the alloy. The influence of surface cracking and necking of the specimens on fracture was negligible.

As shown in Figure 10, increasing the nitrogen content reduced the extent of micro-cracking (number x length in 0.010 square inch of sample) for a given time of testing. This is the same as stating that the extent of micro-cracking was reduced for a given amount of creep because, with the exception of the 0.003-percent nitrogen heat tested at 28,000 psi, the curves of Figure 10 are based on tests with the stress varied to give the same creep rate during secondary creep. At 140 hours, while all samples, regardless of nitrogen level, were still in secondary creep at similar creep rates, the extent of micro-cracking was 0.090-inch per 0.010 square inch with 0.003-percent nitrogen, 0.019-inch per 0.010 square inch with 0.013-percent nitrogen, 0.009-inch per 0.010 square inch with 0.027-percent nitrogen, and zero with 0.034-percent nitrogen. Figure 10 also shows that at 28,000 psi the 0.003-percent nitrogen heat developed a few micro-cracks as soon as the load was applied, whereas the 0.034-percent nitrogen heat required more than 140 hours of creep under this stress before micro-cracks became visible.

Once cracks become visible the rate of growth seemed to be equal for all nitrogen levels (Figure 11). However, both Figures 10 and 11 indicate that the micro-cracks had to grow to longer lengths to cause fracture. The number of micro-cracks (Figure 12) for any specific time of exposure to creep under stresses giving equal secondary creep rates decreased with increasing nitrogen. This evidence indicates that a controlling factor influencing creep-rupture properties was the number of micro-cracks and is further substantiated by noting that the total

extent of micro-cracking was nearly constant at fracture (Figure 10). In fact, the extent of micro-cracking governed the life. When the extent of micro-cracking was plotted against the percentage of rupture life used the data for all the nitrogen levels were similar (Figure 13).

All these data point to the time of nucleation of micro-cracks and the number nucleated being the controlling factors. Growth entered into the rupture life only in that a longer time for rupture was required when the number of micro-cracks was reduced by increasing the nitrogen. There are, however, a number of limitations to these data with the relatively large size to which the micro-cracks had to grow before they could be counted and measured the most severe. No information is available on the nucleation and growth of micro-cracks in the early stages of their formation. The determination of the number and size of the micro-cracks was complicated because linking of micro-cracks occurred at the same time new micro-cracks were being formed.

As far as could be ascertained from the data, the initiation of tertiary creep was mainly controlled by the degree of micro-cracking. It appears, therefore, that increasing nitrogen increased rupture life (when creep rates were kept constant) by the following combined effects:

1. Delay of the initiation of tertiary creep by increasing the time for the appearance of micro-cracks.
2. Reduction of the rate of tertiary creep and an increase in the duration of tertiary creep by reducing the number of growing micro-cracks.

The rupture properties of the heats were evaluated in terms of rupture time at a constant stress of 28,000 psi (Figure 5). At this stress the 0.003-percent nitrogen heat developed micro-cracks more

rapidly than occurred in the constant creep rate evaluation of this heat. This is probably due to either or both the increased creep rate and higher stress. The influence of nitrogen on the micro-cracking characteristics governed the relative rupture lives of the higher nitrogen heats.

Others[46,47] have observed that intergranular rupture in slow creep occurs through the formation and slow growth of "holes" (intergranular micro-cracks, normal to the tensile stress) to a "critical size" which then propagates immediately to rupture. However, recognizable micro-cracks have occurred in some cases during transient creep[46], in other cases in second stage creep[46,55,56] and in still other cases not until tertiary creep[47,57,58]. These observations are not surprising considering that in this study the nucleation of micro-cracks was delayed from early in transient creep (i.e. on loading) to late in second stage creep by increasing nitrogen.

Intergranular Precipitation

Since micro-cracks appeared to be formed at the grain boundary particle-matrix interface, a study of the type and mode of precipitation of intergranular particles was performed.

Precipitation of particles in the grain boundaries occurred in all heats during aging at 1350°F, 1400°F and 1450°F after solution treatment at 2000°F. The increase of nitrogen caused the intergranular precipitation to differ in several respects (Table V). In the higher nitrogen heats a continuous network of fine particles formed in the grain boundaries after aging between 1 and 24 hours depending on aging temperature (Figure 14). The precipitates in the grain boundaries of the 0.003-percent nitrogen heat never became continuous even after

1000 hours aging (Figure 14). The grain boundary precipitates formed both as fine discrete particles and cellular structures (Figure 15). The cellular type of precipitate was observed most frequently in the 0.003-percent nitrogen heat.

After a continuous network of the particles developed in the grain boundaries of the heats with 0.013-, 0.027- and 0.034-percent nitrogen a further precipitation of extremely fine particles occurred in regions adjacent to the boundaries (Table V, Figure 14). This precipitation did not occur in the 0.003-percent nitrogen heat. Although these particles were not positively identified, their reaction to polishing and etching was similar to that exhibited by the intergranular particles. Furthermore, the fact that this precipitation occurred near the grain boundaries, but did not occur until a continuous network of precipitates formed in the boundaries, suggests that this may be a further precipitation of the same material forming the intergranular particles.

The lowest temperature for the complete solution of the intergranular particles increased from 1575°F at 0.003-percent nitrogen to 1925°F at 0.034-percent (Table VI).

In order to investigate further the influence of nitrogen on the nature of the intergranular precipitates, the type of particles was studied by x-ray diffraction of extracted residues. The quantitative data are shown in Tables VII and VIII, and Figure 16, and the limitations of these data are discussed later. After aging the 0.003-percent nitrogen heat 24 hours at 1450°F, the predominant type of precipitate was $Cr_{23}C_6$ with some Cr_7C_3 present. Increasing the nitrogen content to 0.013-percent and above (at the same aging conditions) resulted in a considerable increase in the ratio of Cr_7C_3 to $Cr_{23}C_6$. In fact,the intergranular precipitate seemed to be mostly Cr_7C_3. The differences between the

higher nitrogen heats with respect to the amount of Cr_7C_3 and $Cr_{23}C_6$ present were much more difficult to discern. A comparison of the diffraction patterns of the higher nitrogen heats to each other and to the pattern of the 0.013-percent nitrogen heat indicated that the ratio of Cr_7C_3 to $Cr_{23}C_6$ was further enhanced by nitrogen additions above 0.013-percent. However, this increase was considerably smaller than found for the first nitrogen addition. Electron diffraction studies of precipitate particles using extraction replicas yielded diffraction patterns which indexed for $Cr_{23}C_6$ in some cases and Cr_7C_3 in others. However, because only a few diffraction spots were obtained on any given selected-area diffraction pattern, these identifications were not completely trustworthy.

Although these precipitates were identified as Cr_7C_3 and $Cr_{23}C_6$, it should be pointed out that substitution of nitrogen for carbon could occur in these carbides and be extremely difficult to detect. There was no consistent evidence from the x-ray diffraction data that this had occurred, but because of the similarity of the atomic diameter of nitrogen and carbon atoms a limited substitution of nitrogen could occur and not be detected in the x-ray diffraction patterns.

It appears that the cellular structures were $Cr_{23}C_6$ since in the 0.003-percent nitrogen heat the amount of $Cr_{23}C_6$ in the extracts and the amount of cellular precipitates in the microstructure were higher than found in the other heats. Support for this can be found in the literature. Mihalisin[22] found that a cellular-type precipitate in a very similar alloy (Nimonic 80) was $M_{23}C_6$ (where M = Cr and/or Mn, Fe). It is also clear from the literature that $M_{23}C_6$ - type carbides can occur as discrete particles as well as cellular structures.

The decreased micro-cracking associated with increased nitrogen seemed to be related to the change of the predominant type of carbide from $Cr_{23}C_6$ to Cr_7C_3. Hence, it appears that $Cr_{23}C_6$ particles acted as easy sites for the nucleation of micro-cracks, possibly because of poor bonding. In general, the literature supports the conclusion. Mihalisin[22] reported that the presence of $M_{23}C_6$ -type carbides in a Nimonic alloy, especially with a cellular distribution, was conducive to poor rupture properties. On the other hand, Betteridge and Franklin[21] showed that, in a similar alloy, better rupture properties were obtained when Cr_7C_3 was precipitated in the grain boundaries, especially if this precipitation formed a rather continuous network of discrete particles. Similar effects from cellular structures have been noted in other alloys. Roberts[59] and Sully[60] found that cellular precipitation in magnesium - aluminum and aluminum-copper alloys caused poor rupture properties. Regarding the role of precipitate particles on micro-crack formation in general, Resnick and Seigle[48] established that ZnO particles were heterogeneous nuclei for micro-cracks in α-brass, and Machlin[49] showed that particle-matrix bonding was important in the nucleation of micro-cracks.

The mechanism of nucleation and growth of these micro-cracks is not clear. Several authors[46,47,48,49,50] have proposed condensation of vacancies formed during creep by dislocation movements. Others[51,52,53] maintain that local stress concentrations are the cause. Eborall[54] proposed a combination of both. Regardless of the actual mechanism, it is quite clear that the type of precipitate and/or its form is extremely important in the formation of micro-cracks.

Although it appears relatively well established that the type of carbide in the grain boundary was responsible for the change in ease of

micro-cracking, the influence of nitrogen on this change in carbide needs further consideration. An excellent instance in which nitrogen did have a marked influence on the precipitation of carbide-type particles was found when Heat 1 (0.020 carbon, 0.003 nitrogen) was compared to Heat 3 (0.025 carbon, 0.027 nitrogen) with the same heat treatment. Although the carbon contents are almost the same, the amount of intergranular precipitation in Heat 3 was considerably more than that found in Heat 1 (Figure 14). Furthermore, the temperature for complete solution of these intergranular carbides was increased markedly from 1575°F in Heat 1 to 1825°F in Heat 3. In general, increased nitrogen acted similar to increased carbon insofar as its effect on solution and precipitation characteristics of carbide-type particles was concerned. Lane and Grant[61] also found the effect of nitrogen on the microstructure of the several alloys they examined to be similar to that of an increase in carbon.

The effect of nitrogen on intergranular precipitation could be due either to a change in the solubility of carbon in the matrix, or to the substitution of nitrogen for carbon in either or both of the existing carbides. In either case the equilibrium relationship of these carbides could be changed thereby causing one to be formed in preference to the other. Both of these possibilities can be justified by the data. Consequently, it is not clear which is the correct explanation, and indeed, it is quite possible that both occurred.

Interpretation of Other Microstructural Changes

There were other microstructural changes that could possibly effect creep-rupture properties, and these will be considered in detail

in the following sections.

Influence of γ' on Creep Resistance

Considerable effort was made to determine if the observed effects on creep resistance were due to a change in the γ' precipitation.

The first step in this study was to verify that the general precipitate was γ', $Ni_3(Al, Ti)$. Electron diffraction spots from particles on an extraction replica were indexed for γ' with an average lattice parameter of 3.57 Å (Figure 17).

During air cooling from the rolling temperatures, γ' precipitated in all heats. Experiments showed that this was dissolved by heating to 1600°F (Table VI). Heating to 1550°F did not dissolve all the γ'. The experiments were not precise enough to determine if there was a difference in solution temperature within the 50°F range as a result of variations in chemical composition.

Aging experiments at 1350°F, 1400°F and 1450°F demonstrated that the number of γ' particles per unit area decreased with time and at equal aging times decreased with aging temperature (Figure 18,19,20). For any particular treatment, at all aging temperatures, there were slightly fewer γ' particles per unit area in the 0.003-percent nitrogen heat than in the three heats with higher nitrogen. At first, it appeared that the increase in γ' particle density offered a satisfactory explanation for the increased creep resistance associated with the same increase in nitrogen content.

However, this conclusion was questionable since, as established earlier, all heats had creep-rupture properties relatively independent of prior aging temperature. The independence of aging suggested that within certain limits creep resistance was relatively insensitive to

changes in γ' precipitation. To help clarify this question the relation of creep resistance to γ' precipitation was studied in more detail.

The dispersion of γ' particles (average distance between particles) appeared to be the important consideration when it was assumed that theory of dispersion hardening as put forth by Mott and Nabarro[62] and its extension by Orowan[63] was applicable in its general sense to resistance to creep. The γ' dispersion of the 0.003-percent nitrogen heat aged 24 hours at 1400°F after solution treatment at 2000°F was 0.040 microns. The γ' dispersion of the higher nitrogen heats aged 24 hours at 1450°F after solution treatment at 2000°F was similar--0.036 microns (Table IX). On the basis of γ' dispersion, the minimum secondary creep rate of specimens heat treated to these conditions should have been similar. Actually, the secondary creep rates were quite different (Figure 1). Further evaluation of the influence of γ' dispersion on secondary creep rate was made by heat treating the 0.003-percent nitrogen heat 24 hours at 1450°F after solution treatment at 2000°F (dispersion of γ' particles--0.073 microns, Table IX). Comparison of this heat aged at 1400°F and 1450°F suggested that the secondary creep rates would be higher with a prior aging treatment at 1450°F since the γ' spacing was considerably larger. However, the secondary creep rates were similar (Figure 1). There is further evidence that something other than the difference in γ' precipitation caused the creep resistance to be increased. Specimens of the 0.013- and 0.034-percent nitrogen heats were given a special heat treatment which resulted in the nitrogen being precipitated (for details of treatment see page 43). This treatment produced the same γ' precipitation obtained in these heats with the usual treatment. Although the γ' precipitation was the same, the creep rate of these specimens (Table XI) was increased markedly, thus

indicating that some other structural change was controlling the creep rate of these heats.

These comparisons suggest very strongly that differences in γ' dispersion, at least within the limits considered, had little influence on minimum secondary creep rate. It is recognized that this argument could be challenged on the basis of the precision of the measurement of γ' dispersion. However, further analyses using γ' density (the number of particles per unit area) in place of γ' dispersion produced the same results. Although it appears that γ' density has less fundamental significance, this measurement is the easiest to perform and is most commonly used for comparisons of this type[17].

It is evident from these analyses that the differences in density or dispersion developed in the experimental heats prior to creep-rupture testing could not account for the increased creep resistance of the three higher nitrogen heats.

That mechanical properties were relatively insensitive to small changes in γ' density or dispersion was also evidenced in the change of hardness during aging of the experimental heats at 1450°F (Table X). Maximum hardness was reached after 24 hours agings, and this hardness did not change much on further aging to 1000 hours (Figure 20). Yet, as shown in Figure 20, the number of γ' particles per unit area decreased and the distance between particles increased slowly but continually with aging longer than 24 hours. Hence, there appears to be a range of γ' density or dispersion over which mechanical properties are relatively unaffected. Under these circumstances, the level of hardness attained during aging of these heats (Figure 20) is very difficult to explain. The difference in hardness between the 0.003- and 0.034-percent nitrogen heats during aging was similar to the differ-

ence in hardness of these heats after solution treatment. Since the titanium and aluminum contents were similar, it appeared that the difference in hardness was due to nitrogen in solution. On the other hand, the 0.013- and 0.027-percent nitrogen heats had similar hardness in aging, but this hardness was higher than the other heats. The increased hardness of these heats might be related to the higher titanium and aluminum content but cannot be explained on the basis of γ' density or dispersion alone since this was similar to that found in the 0.034-percent nitrogen heat. No consistent explanation can be found for these data and it is quite obvious that the aging process in these heats is a complex phenomenon.

Whether the increase in the number of γ' particles per unit area in the higher nitrogen heats was related to the increased nitrogen content, or to the small changes in titanium and aluminum content, or a combination of both, is an exceedingly difficult question to answer. It could be argued that nitrogen "atmosphere" around dislocations nucleated the precipitate because of its probable close association with titanium and aluminum in the matrix. It is also possible that the addition of small amounts of nitrogen could influence the γ' reaction through an effect on the equilibrium phase relationships. Although these are possibilities, the lack of information make even qualitative discussions difficult.

It is also possible that the small differences in chromium, titanium and aluminum content caused the γ' density to be increased; however, quantitative discussion of this point is difficult. Although the extents of the γ and γ' phase fields at 1382°F within the pseudo-ternary section Ni_3Cr - Ni_3Ti - Ni_3Al (75 atomic percent nickel) have been established within $\pm 1/2$ atomic percent by Taylor[14], the application of

this diagram to the heats with varying nitrogen is of dubious value for two major reasons. First, as pointed out by Taylor, the tie-lines linking the γ and γ' phases in equilibrium are not necessarily in the plane of the section presented. Consequently, the uses of these tie-lines to estimate the amount of γ and γ' that should be present at equilibrium may result in errors. Secondly, the nickel content of the 0.003-percent nitrogen heat (about 78 atomic percent) is enough different from the 75-percent nickel, for which the section was established, to suggest that consideration of this heat in light of the published diagram is open to question.

When the pseudo-ternary section was used to calculate the amount of γ', the calculated figures were greatest for the 0.003-percent nitrogen heat and lowest for the 0.034-percent nitrogen heat in contrast to the opposite variation in the actual heats. However, in view of the preceding discussion, these data cannot be construed to mean that nitrogen had changed the phase relationships. It is quite obvious at this point that there are several possibilities for the explanation of the increased γ' density for the higher nitrogen heats, but in view of the lack of knowledge the true explanation cannot be established.

Influence of Micro-Cracking on Creep Resistance

Several authors[50,55] attribute tertiary creep and rupture to a gradual destruction of the metal by micro-cracking. This implies that micro-cracking raises creep rate and limits life and ductility. Hence, the explanation of the higher creep rate of the 0.003-percent nitrogen heat might exist in the rate of formation and growth of micro-cracks.

This question can be resolved by considering the extent of micro-cracking in relation to creep rate during creep-rupture testing of the

experimental heats. Several comparisons of the data of Figures 4 and 10 will illustrate the effect of micro-cracking on creep rate during second-stage creep. If micro-cracking had a marked influence of second-stage creep rate, it would be expected that the micro-cracking characteristics during second-stage creep of the 0.013-, 0.027- and 0.034-percent nitrogen heats were similar since the second-stage creep rates of these heats were similar (Figure 4). If micro-cracks were formed during this period of creep and effectively increased the creep rate, the creep curves should not show a region of constant creep rate but should show a curve of continually increasing creep rate. Actually, as shown in Figure 4, the creep curves did have a region of constant creep rate, and, as shown in Figure 10, micro-cracking began during second stage creep in all heats but was initiated after more creep time in the high nitrogen heats. Hence, since micro-cracking did occur in second-stage creep and the creep rate was changed, it appears that micro-cracking does not markedly influence second stage creep of the higher nitrogen heats. This does not completely answer the question of the relationship between micro-cracking and the relatively high secondary creep rate of the 0.003-percent nitrogen heat at 28,000 psi. However, quantitative data from Figure 10 will further clarify the problem.

During 100 hours of second-stage creep at similar secondary creep rates the extent of micro-cracking increased from 0.0 (estimated) to 0.075 inch per 0.010 square inch (estimate) in the 0.003-percent nitrogen heat, from 0.019- to 0.090-inch per 0.010 square inch in the 0.013-percent nitrogen heat, from 0.008- to 0.040-inch per 0.010 square inch in the 0.027-percent nitrogen heat, from 0.0 to 0.020-inch in the 0.034-percent nitrogen heat. Consequently, these

data show that the extent of micro-cracking can change from 0.0 to 0.090-inch per 0.010 square inch without affecting minimum secondary creep rate.

Therefore, in order to account for the second stage creep rate of the 0.003-percent nitrogen heat at 28,000 psi by micro-cracking, the extent of micro-cracking developed on loading a specimen from this heat should be greater than 0.090 inch per 0.010 square inch because this heat immediately crept at a higher rate than the others. However, as shown in Figure 10, this value was not reached on loading the sample. Furthermore, this heat was in creep at its higher creep rate for at least 30 hours before the extent of micro-cracking exceeded this value.

Therefore, it appears that the formation of micro-cracks on loading the 0.003-percent nitrogen heat and their subsequent rapid growth cannot account for the higher creep rate (decreased creep resistance) in second-stage creep in comparison to the higher nitrogen heats.

Influence of Intragranular Precipitation on Creep Resistance

After aging the 0.013-, 0.027- and 0.034-percent nitrogen heats 100 hours at 1450°F a new, randomly distributed precipitate was observed within the grains. It was not found in the 0.003-percent nitrogen heat. At first, it was thought that this was a further precipitation of the carbides that occurred in the earlier stages of aging. However, the new phase was found to occur quite often as growths on the original massive Ti(CN) present in the alloy (Figure 21). Furthermore, a re-solution treatment of these aged samples at 1700°F or 2000°F showed that the particles did not go into solution (Figure 21).

This intragranular precipitation appeared to be evidenced in the change in the lattice parameter of the matrix during aging at 1450°F (Table X). The relationship of nitrogen and the decrease in lattice parameter of the matrix during aging is difficult to assess because γ', $Ni_3(Al, Ti)$, also precipitates during aging. Hence, several elements are removed from the matrix which probably influence lattice parameter. However, as shown in Figure 22, the originally higher lattice parameters of the 0.013- and 0.027-percent nitrogen heats show a rather sharp decrease after 100 hours aging which was not observed in the 0.003-percent nitrogen heat. In fact, this coincides with the observance of the intragranular precipitate in the matrix and on Ti(CN) particles (Table V).

It appeared that the precipitation of this new phase resulted in the removal from solid solution of an element which had a relatively large influence on lattice parameter. There is considerable evidence in these data that this precipitate contained nitrogen. This precipitation did not occur in the low nitrogen heat, while in the higher nitrogen heats it occurred quite often as growths on or as patches around the massive Ti(CN). The decrease in lattice parameter with the occurrence of this phase also strongly suggests that nitrogen was removed from solution since, as mentioned previously, nitrogen was found to increase lattice parameter in solution treated samples. This was especially evident in the decrease of lattice parameter of the 0.013- and 0.027-percent to a value similar to the 0.003-percent nitrogen heat after 1000 hours aging. The resistance to re-solution in the matrix suggests the existence of a very stable compound, as many nitrides are known to be.

It, therefore, appeared that nitrogen was removed from solution by long aging, and consequently, this would be expected to lead to decreased creep resistance. To verify this, specimens of the 0.013- and 0.034-percent nitrogen heats were aged 1000 hours at 1450°F to develop this condition. These samples were re-solution treated at 1700°F and aged 24 hours at 1450°F to establish the same γ' distribution that occurred on aging 24 hours at 1450°F after solution treatment at 2000°F. The second-stage creep rate of these specimens was increased considerably (Table XI). Consequently, this is considered further evidence that nitrogen was removed from solution by long aging treatments and that its removal caused the creep resistance to be decreased.

The 1000-hour aging treatment also caused the formation of more $Cr_{23}C_6$-type carbide than was present after the usual 24 hour aging treatment (Table VIII). It appeared that the ratio of Cr_7C_3 to $Cr_{23}C_6$-type carbide was higher in the higher nitrogen heats even after this exposure than found in the 0.003-percent nitrogen heat with the usual treatment (compare x-ray diffraction patterns of Table VII). Thus, the rupture life would be expected to decrease but not to the value of the 0.003-percent nitrogen heat.

A further evaluation of the relative effects of solution nitrogen and intergranular precipitation on creep-rupture properties was obtained. Specimens of the 0.013- and 0.027-percent nitrogen heats were solution treated 4 hours at 2000°F, transferred directly to a furnace at 1700°F for 24 hours and water quenched. These specimens were then aged 24 hours at 1450°F. The treatment of 24 hours at 1700°F developed a comparatively coarse carbide structure in the grain boundaries (Figure 23), which was identified as predominantly

Cr_7C_3 (Tables VII and VIII). Aging 24 hours at 1450°F resulted in a γ' structure similar to that formed on aging 24 hours at 1450°F after solution treatment at 2000°F. The aging treatment also caused a further precipitation of intergranular particles which were probably both Cr_7C_3- and $Cr_{23}C_6$-type carbides. No other precipitation occurred to suggest that nitrogen was removed from solution during this heat treatment as occurred during the prolonged aging treatment. Consequently, specimens subjected to this treatment should exhibit second-stage creep rates similar to those obtained from samples aged 24 hours at 1450°F after solution treatment at 2000°F. Results from creep-rupture tests show that the creep rates were similar (Table XI).

The rupture properties of specimens given this treatment (Table XI), were similar to those obtained from samples aged 24 hours at 1450°F after solution treatment at 2000°F (Table III). In one case a rather discontinuous network of large and small carbides formed and in the other case a continuous network of fine carbides formed in the grain boundaries. Consequently, there was no evidence that changing the size and distribution of the precipitates in the grain boundaries altered the rupture life.

Influence of Variations in Chemical Composition on Lattice Parameter

As mentioned in a previous section the increase in lattice parameter of solution treated samples could not be accounted for by variations of chemical composition other than nitrogen in solution. However, because this interpretation of the effect of nitrogen in solution on lattice parameter might be questioned on the basis of variation

in the amount of chromium, titanium, aluminum and carbon, this point should be considered in detail.

Variations of Chromium, Titanium and Aluminum

The influence of the changes in chromium, titanium and aluminum content on the lattice parameter will be considered first, using the data of Taylor[14] on the quaternary nickel - chromium - titanium - aluminum system. From the equi-parameter curves of Taylor the lattice parameter of solution treated samples of the heats used in this investigation should decrease in the following order: heat 1 - 3.554Å, heat 2 - 3.553Å, heat 3 - 3.550Å, heat 4 - 3.5623Å. The actual lattice parameters increased from 3.5623Å in the 0.003-percent nitrogen heat to 3.5658Å in the 0.034-percent nitrogen heat (Table V).

There was a rather large discrepancy (about 0.01Å) between the lattice parameters determined in this investigation and those determined by Taylor. This same discrepancy was noted when the data of Kurdyumov and Travina[37] were compared to Taylor's data. The reason for the consistent discrepancy between Taylor's work and others was not clear. The purity level of the alloys may be a factor. Taylor also used a smaller diffraction camera and a different radiation than were used in this investigation. He did not state the method used to determine a_o value. However, it is probably safe to assume that the work of Taylor was at least self-consistent.

Further attempts to evaluate the relative effects of variations in chromium, titanium and aluminum content on the lattice parameter were made using Vegard's law. It was first applied to the data of Taylor and Floyd[12] and Taylor[14] to determine if changes in these elements in the range considered would follow Vegard's law. It was

found that the change in lattice parameter with atomic percent of chromium, titanium and aluminum did not follow the law; and moreover, the calculation suggested a relatively large negative deviation from it. Application of Vegard's law to the present data proved unsatisfactory. When it was assumed that only the variations in aluminum were important to the lattice parameters, calculated lattice parameters, using Vegard's law, were in all cases smaller than the actual values. This suggested that variations in other elements were also important. The change of lattice parameter predicted from variations of all three elements (chromium, titanium and aluminum) were inconsistent, some cases being high and others low. However, this was not surprising since it did not appear that Vegard's law was applicable to the quaternary alloy.

Since the lattice parameters were increased, when, from Taylor's data they should be decreased, it appears that either nitrogen or carbon or both caused the increase of lattice parameter.

Variations of Carbon

There were variations in carbon content which, although relatively small, might influence the lattice parameter of solution treated samples. However, experiments showed that while the lattice parameter was not changed by solution treatment at temperatures between 1600°F and 2000°F (Table VI), the intergranular carbides did go into solution. These data indicate that solution of carbon in the matrix had no appreciable effect on the lattice parameter. Further confirmation was obtained when specimens of the experimental heats were heated to 2000°F, held 4 hours, transferred directly to a furnace at 1700°F, held 24 hours, and water quenched. Although the actual amount of

carbon removed from solution by this treatment is not known, the intergranular precipitation of carbide was quite extensive for the higher nitrogen heats; but,as expected from previous data, there was no carbide precipitation in the 0.003-percent nitrogen heat (Figure 23). The lattice parameter and hardness (Table VI) were similar to those obtained from samples solution treated 4 hours at 2000°F and water quenched in which the grain boundaries were completely free of these carbides (Figure 7). Thus, as suggested from the initial experiments, the lattice parameter of the matrix was relatively unaffected by changes in carbon content, at least for the range covered. It should be recognized that a small change in lattice parameter could have occurred and gone undetected because of the reproducibility of the lattice parameter measurements.

Variations of Nitrogen

As a result of the previous discussions it is evident that the increased lattice parameter can best be accounted for by nitrogen in solution expanding the lattice. On the surface this argument may not seem reasonable since carbon, an atom very similar in size to nitrogen, had little or not detectable effect. However, reference to the literature will suggest that such a situation could indeed exist.

Roberts[64] summarized the data on the effect of carbon from 0.7 to 1.5 weight percent and Jack[65] studied the effect of nitrogen from 0.8 to 2.3 weight percent on the lattice parameter of iron (austenite). The range of 0 to 0.65 weight percent carbon or nitrogen was not covered in these investigations. However, these data can be used if a linear relationships is assumed between lattice parameter and percent carbon or nitrogen. On comparing the data on the basis of change in

lattice parameter per atomic percent of carbon or nitrogen, it was evident that the influence of nitrogen on lattice parameter of iron (austenite) is about double that of carbon. Jack[47] also pointed out that nitrogen had a larger effect than carbon on the lattice parameter of iron (austenite) above 0.8 weight percent of these elements. Trillat[66] found that the lattice parameter of pure nickel increased from 3.52 to 3.72Å with increased nitrogen to a point where saturation occurred and the hexagonal Ni_3N phase formed. From these data it was evident that nitrogen in pure nickel had a larger influence on lattice parameter (about 50 percent larger) than did nitrogen in iron (austenite). It was recognized that actual data in the range 0 to 0.5-weight percent carbon and nitrogen would be more useful than the extrapolation used above. It was hoped that such data could be found in relation to austenitic stainless steels, but a search of the literature for this information proved unsuccessful.

Since the lattice parameter of solution treated samples could be reproduced to only $\pm$0.0004Å, changes in lattice parameter below this limit could not be successfully detected. Consequently, in view of the relative effects of carbon and nitrogen on lattice parameter as established above, it is possible that a small change in lattice parameter by carbon went undetected while a slightly larger effect from nitrogen was detected. This appears especially probable because of the low content of carbon and nitrogen in the heats.

Limitation of X-Ray Diffraction Identification

It is evident from the x-ray diffraction data in Tables VII and VIII that two problems exist which complicated the analysis of these patterns. First, only the 2.29, 1.18 and 1.17 "d" value diffraction lines for Cr_7C_3 and the 2.38 and 2.17 "d" value diffraction lines for $Cr_{23}C_6$ appeared to be completely free from interference with the same or similar diffraction lines of other compounds present in the alloy. Secondly, the diffraction lines of these carbides were very weak. Consequently, the analyses were based on only a few weak diffraction lines.

The determination of the relative amounts of the carbides was limited by the intensity measurements. Although the analyses were based on intensity comparisons from visual intensity classifications, confirmation that these classifications were consistent within any particular film and not biased by the observer was obtained from the results of microphotometer traces of several films (Table VII and VIII and Figure 16). It should be recalled, however, that in all cases these diffraction lines were quite weak.

The analyses of the relative amounts of Cr_7C_3 and $Cr_{23}C_6$ in the 0.003-percent nitrogen heat in comparison to the 0.013-percent nitrogen heat after the same thermal treatment was not difficult to carry out because the differences in intensities were fairly large even though the diffraction lines were weak (Table VII). Evidence that these analyses are based on sound data was found in two features of the data. Duplicate extracts yielded similiar x-ray diffraction patterns (Table VIII) and secondly, the same results were reached from extracts produced by the bromine-extraction technique (Table VII) or the

hydrochloric acid extraction technique (Table VIII).

A much more difficult consideration was the change in carbide ratio between the 0.013-percent nitrogen heat and the higher nitrogen heats. Careful study of the relative intensities of the diffraction lines of these patterns suggests that a further increase in the ratio of Cr_7C_3 to $Cr_{23}C_6$ occurred but because of the weakness of the lines it is quite difficult to obtain a quantitative measure of the increase. Qualitatively, it certainly does not appear to be as large a change as that associated with the first addition of nitrogen.

Generality of Results

The inability to establish unequivocally the most basic mechanism by which nitrogen increased creep resistance makes the results more general rather than specific. The results can, however, be analyzed in terms of existing theories and areas of further research defined in a manner which was not possible before the results of this investigation became available.

The experimental evidence established that increased creep resistance was associated with increased nitrogen in solution before the creep-rupture tests were started. It could be hypothesized that the strengthening effect of nitrogen is due to the formation of Cottrell "atmospheres" of nitrogen atoms which impede flow. It is probable that such atmospheres do form at lower temperatures, and this appears to be the explanation for the strain aging behavior at 900°F. However, it is difficult to accept the possibility of the formation of an "atmosphere" of nitrogen atoms that could impede flow at the testing temperatures (1350°F), unless it was stabilized in some manner. It

can be hypothesized that this could occur due to the tendency for the nitrogen to combine with titanium, aluminum or chromium to form nitrides. Thus,the effectiveness of nitrogen appears to be associated with either pre-compound stabilization of the nitrogen or by very small actual precipitates in the dislocations. The prolonged aging treatment indicated that at least part of the nitrogen could be removed from solution as a nitride of an unidentified type. However, when this precipitate was observed,creep resistance was low. Consequently, when the nitrides had attained a recognizable size,they did not appear to be effective for increased creep resistance. It could have been effective, however,in the earlier stages of its formation. The results of this investigation indicate that basic research designed to clarify the mechanism of creep strengthening from interstitial elements in the presence of other elements which tend to combine with them to form compounds is desirable in the development of the basic theory of alloying for creep resistance. Such an investigation would be best carried out in the absence of other precipitation such as the γ' precipitation that occurs in this alloy.

Areas of needed basic research are also defined by the ability of nitrogen to change the type of intergranular precipitate from $Cr_{23}C_6$ to Cr_7C_3. The data obtained suggest that this could either be due to reduced carbon solubility from nitrogen or to nitrogen substitut ed for carbon in the compounds. The way in which nitrogen does this needs to be established. It can be pointed out that other elements such as a boron and molybdenum also change the type of precipitate by unclarified means. It is perhaps more important that research be initiated to define the reason for the greater tendency for cracks to initiate at $Cr_{23}C_6$ type precipitates. The data suggest that

the cohesion between this precipitate and the matrix is much less than for Cr_7C_3.

It appears that nitrogen will be effective for increased creep resistance in alloys in which nitrogen can remain active in the matrix. The effectiveness of the nitrogen will depend on the amount present, at least over a range of nitrogen contents. The amount of nitrogen that can actively interfere with the creep process should depend considerably on the addition of other alloying elements and prior heat treatment. Furthermore, the increase in creep-resistance will be found only over the range of temperatures for which the nitrogen can materially interfere with the flow process of creep.

It is expected that the effect of nitrogen on rupture life will depend very markedly on additions of other alloying constituents. For instance, additions of Mo[19] are known to promote the formation of either or both $M_{23}C_6$ or M_6C. Thus, the effectiveness of nitrogen in promoting the formation of Cr_7C_3 may be completely suppressed with these additions.

The mechanism of creep and fracture can be expected to vary with stress and test temperature. Thus,at other stresses and test temperatures nitrogen may no longer be effective or may even become more effective for improving creep resistance. Under conditions of testing which favor high creep rates the mode of formation and propagation of micro-cracks may be quite different. Thus, the influence of grain boundary - matrix relationships in micro-crack formation may become materially changed.

Even under the same conditions of testing as used in this investigation major changes in the amount of precipitation hardening elements may lead to marked changes in grain boundary characteristics, and

hence, to the effectiveness of nitrogen. As has been found in other investigations[30,67], higher titanium and aluminum contents lead to marked agglomeration of γ' around the carbides in the grain boundaries. Consequently, the micro-cracking tendencies may be materially changed.

CONCLUSIONS

An experimental study was conducted to determine the effects of nitrogen on high temperature properties of a 78 Ni - 19 Cr - 2 Ti - 1 Al alloy subject to hardening by precipitation of $Ni_3(Al, Ti)$. It was found that nitrogen markedly improves creep-rupture properties at 1350°F. Raising nitrogen from 0.003 to 0.013 percent effectively increases creep resistance. At the same time, nitrogen up to 0.034 percent increases the resistance to fracture by delaying the initiation of an increasing the time and deformation in tertiary creep. The increased resistance to creep and fracture results in increased rupture life with the most marked effect found from increasing the nitrogen from 0.003 to 0.013 percent. It was evident that the effective nitrogen in all heats was less than the analyzed nitrogen since this included nitrogen from inactive Ti(CN).

Evidence from structural investigations indicates that there are two major effects caused by nitrogen which account for the increase in creep-rupture properties. The increase in creep resistance is best associated with the increase of nitrogen in solution in the alloy at the start of the creep-rupture tests. Secondly, the increase in the resistance to tertiary creep and fracture is due to a reduction in the susceptibility to micro-cracking. Indications are that this results from a change in the major type of intergranular precipitate from $Cr_{23}C_6$ - to Cr_7C_3 type compounds which form prior to and during creep-rupture testing.

Some possible causes for the influence of nitrogen on the grain boundary precipitates are discussed. It seems most probable that nitrogen decreases the solubility of carbon in the matrix or substi-

utes into the intergranular compounds or both, thereby causing the formation of more Cr_7C_3-type compounds.

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TABLE I

CHEMICAL ANALYSES OF RAW MATERIALS

Material	(Weight Percent)										
	Ni	Cr	Al	Ti	Fe	Si	C	O	N	S	Cu
Electrolytic Nickel	Bal	--	--	--	0.02	--	Trace	--	--	Trace	0.01
Shieldalloy Chromium	--	Bal	0.06	--	0.28	--	0.05	--	--	0.025	--
Aluminum pig	--	--	Bal	--	0.001	0.002	--	--	--	--	0.003
Commercially Pure Titanium	--	--	--	Bal	0.20	--	0.02	0.12	0.012	--	--
Chromium Nitride	No analysis given - similar to CrN[1]										
Spectrographic Grade Carbon											

1. An x-ray diffraction pattern of the powder yielded diffraction lines in agreement with cubic CrN. No other lines were detected.

TABLE II

CHEMICAL ANALYSES OF EXPERIMENTAL HEATS

(Weight Percent)

Heat	N	Ni	Cr	Ti	Al	Si	Mn	C	B	Zr	O
1	.003	78.76	18.15	1.87	1.08	--	.11	.02	< .001	<.01	.0010
2	.013	78.13	18.51	1.93	1.26	.02	.09	.04	< .001	<.01	.0007
3	.027	77.43	19.16	1.92	1.40	--	.04	.025	< .001	<.01	.0008
4	.034	76.81	20.00	1.82	1.17	.02	.09	.05	< .001	<.01	.0008

(Atomic Percent)

Heat	N	Cr	Ti	Al	C
1	.012	19.43	2.17	2.23	.09
2	.052	19.99	2.26	2.62	.19
3	.108	20.65	2.25	2.91	.12
4	.136	21.57	2.13	2.43	.23

TABLE III

CREEP-RUPTURE AND MICRO-CRACK DATA AT 1350°F

(Initial Condition - 4 hours at 2000°F, W. Q. + Aged 24 hours at 1450°F)

Heat	Stress (psi)	Minimum Second Stage Creep Rate (in/in/hr)	Rupture (hours)	Interruption (hours)	Elongation[1] (percent)	Reduction of Area (percent)	Start of Tertiary Creep (hours)	Time in Tertiary Creep (hours)	Number of Micro-cracks[2]	Length of Micro-crack (inch)	Extent of Micro-cracking (Number x Length) (inch)	Fraction of Life[3]
1	28,000	0.865×10^{-5}	98.9	---	0.8	2.6	55	43.9	---	---	---	---
2	28,000	0.597	502.9	---	2.4	2.1	290	212.9	---	---	---	---
3	28,000	0.340	675.0	---	0.8	2.9	350	325.0	---	---	---	---
4	28,000	0.737	695.1	---	1.6	2.7	270	425.1	---	---	---	---
(Initial Condition - 4 hours at 2000°F, W. Q. + Aged 24 hours at 1400°F)												
1	28,000	---	---	on loading	---	---	---	---	41	0.063×10^{-3}	2.58×10^{-3}	---
1	28,000	1.30×10^{-5}	111.0	---	3.2	1.4	60	51	1100	0.325	358.0	1.00
1	28,000	2.32	94.2	---	3.9	2.4	50	44.2	1020	0.311	342.0	1.00
1	24,000	0.345	---	141	0.20	---	100	---	450	0.200	90.0	0.67
1	24,000	0.510	212.1	---	0.8	0.8	120	54.4	1120	0.262	294.0	1.00
2	28,000	0.335	---	141	0.20	---	---	---	160	0.122	19.5	0.27
2	28,000	0.658	---	370	0.41	---	260	---	675	0.293	197.5	0.72
2	28,000	0.452	464.0	---	2.30	2.4	320	144	910	0.330	300.0	1.00
2	28,000	0.323	572.8	---	1.60	2.4	300	272.8	880	0.357	314.0	1.00
3	28,000	0.345	---	141	0.19	---	---	---	96	0.090	8.64	0.21
3	28,000	0.575	---	370	0.40	---	300	---	345	0.250	86.3	0.56
3	28,000	0.385	659.0	---	3.3	3.2	380	279.0	800	0.405	324.0	1.00
3	28,000	0.423	673.8	---	1.6	1.9	360	313.8	820	0.375	308.0	1.00
4	28,000	0.510	---	141	0.21	---	---	---	0	---	---	0.18
4	28,000	0.608	---	370	0.42	---	300	---	250	0.169	42.2	0.48
4	28,000	0.480	923.6	---	2.4	1.9	420	503.6	580	0.537	311.0	1.00
4	28,000	0.540	628.0	---	2.3	2.4	260	368.0	695	0.375	260.0	1.00
(Initial Condition - 4 hours at 2000°F, W. Q. + Aged 24 hours at 1350°F)												
2	28,000	0.410×10^{-5}	542.0	---	3.2	2.5	280	262	---	---	---	---
(Initial Condition - 4 hours at 1700°F, W. Q. + Aged 24 hours at 1400°F)												
1	28,000	1.22×10^{-5}	49.0	---	3.2	1.6	---	---	---	---	---	---
2	28,000	0.680	435.8	---	3.3	1.6	220	215.8	---	---	---	---
3	28,000	0.711	448.1	---	1.6	2.9	300	148.1	---	---	---	---
4	28,000	0.670	851.0	---	3.8	2.2	400	351.0	---	---	---	---

1. Total creep deformation for interrupted tests.
2. Micro-cracks detected at 1000X, number in 0.010 square inch.
3. Ratio of time to interruption to average rupture life of heat.

TABLE IV

STRAIN AGING AND TENSILE TEST DATA AT 900°F

(Initial Condition - 4 hours at 2000°F, W. Q. + 24 hours at 1400°F)

Heat	Height of Serrations Minimum Stress (psi)	Height of Serrations Maximum Stress (psi)	Number of Serrations[1]	Average Elongation Between Serrations[2] (inch)	Tensile Strength (psi)	0.2 Percent Offset Yield Point (psi)	Elongation (percent)	Reduction of Area (percent)
1	900	4800	8	0.0125	115,000	67,900	38.3	48.2
2	2000	6600	12	0.0083	131,000	77,500	32.0	42.3
3	2360	7080	16	0.0062	130,000	79,000	33.8	44.1
4	2360	7080	15	0.0066	120,000	72,100	33.4	42.1

1. Measured in portion of load-elongation curve that was a measure of strain.
2. Arrived at by dividing the number of serrations into the total elongation over which these were observed.

TABLE V

SUMMARY OF THE TIME AND MODE OF PRECIPITATION OF PARTICLES OTHER THAN γ' DURING AGING AT 1350°F AND 1450°F

(Initial Condition - 4 hours at 2000°F, W. Q.)

Heat	Optimum Time for Precipitation in Grain Boundaries[1] (hours)	Time for The Start of Precipitation Adjacent to Grain Boundaries (hours)	Time at which Further Precipitation within the Grains was Observed (hours)
		At 1350°F	
1	---[2]	---[3]	---[3]
2	24	24	1000
3	6-24	24	1000
4	6	6-24	1000
		At 1450°F	
1	---[2]	---[3]	---[3]
2	6-24	24	100
3	6	6	100
4	1-6	6	100

1. Optimum precipitation defined as the time at which a continuous network of particles occurred in the grain boundaries as observed at 500X.
2. This condition did not occur.
3. This precipitation did not occur.

TABLE VI

HARDNESS, LATTICE PARAMETER AND MICROCONSTITUENTS OF SPECIMENS TREATED AT TEMPERATURES FROM 1350° TO 2000°F

Condition		Heat 1			Heat 2			Heat 3			Heat 4		
Temperature (°F)	Time (hours)	Hardness (R_B)	Lattice Parameter (Å)	Micro-constituents	Hardness (R_B)	Lattice Parameter (Å)	Micro-constituents	Hardness (R_B)	Lattice Parameter (Å)	Micro-constituents	Hardness (R_B)	Lattice Parameter (Å)	Micro-constituents
1350	24	97.2	---	γ', C[1], Ti(CN)	101.0	---	γ', C[1], Ti(CN)	100.6	---	γ', C[1], Ti(CN)	100.0	---	γ', C[1], Ti(CN)
1400	24	95.2	---	γ', C[1], Ti(CN)	101.0	---	γ', C[1], Ti(CN)	100.2	---	γ', C[1], Ti(CN)	99.1	---	γ', C[1], Ti(CN)
1450	24	93.5	3.5602	γ', C, Ti(CN)	99.0	3.5630	γ', C, Ti(CN)	98.8	3.5625	γ', C, Ti(CN)	97.6	3.5628	γ', C, Ti(CN)
1500	8	---	---	γ', C, Ti(CN)	---	---	γ', C, Ti(CN)	---	---	γ', C, Ti(CN)	---	---	γ', C, Ti(CN)
1550	8	---	---	γ', C, Ti(CN)	---	---	γ', C, Ti(CN)	---	---	γ', C, Ti(CN)	---	---	γ', C, Ti(CN)
1600	4	73.1	3.5628	Ti(CN)	---	---	C, Ti(CN)	---	---	C, Ti(CN)	---	---	C, Ti(CN)
1700	4	69.0	3.5628[2]	Ti(CN)	72.9	3.5640[2]	C, Ti(CN)	72.0	3.5646[2]	C, Ti(CN)	70.0	3.5658[2]	C, Ti(CN)
1700	24[3]	65.7	---	Ti(CN)	67.8	3.5645	C, Ti(CN)	70.1	3.5640	C, Ti(CN)	68.9	3.5656	C, Ti(CN)
1800	4	66.0	---	Ti(CN)	70.6	3.5635	C, Ti(CN)	70.4	3.5643	C, Ti(CN)	70.3	3.5652	C, Ti(CN)
1850	4	---	---	Ti(CN)	69.0	---	Ti(CN)	68.9	---	Ti(CN)	69.5	---	C, Ti(CN)
1900	4	---	---	Ti(CN)	68.3	---	Ti(CN)	69.0	---	Ti(CN)	68.9	---	C, Ti(CN)
1950	4	---	---	Ti(CN)	---	---	Ti(CN)	---	---	Ti(CN)	68.0	---	Ti(CN)
2000	4	65.5	3.5623[2]	Ti(CN)	68.6	3.5638[2]	Ti(CN)	68.8	3.5643[2]	Ti(CN)	68.5	3.5658[2]	Ti(CN)

1. Intergranular carbide.
2. Average from 3 separate determinations.
3. Held 4 hours at 2000°F and transferred to furnace at 1700°F.

TABLE VII

X-RAY DIFFRACTION DATA FROM BROMINE-METHYL ALCOHOL EXTRACTS

(All d values are in A units; copper radiation)

Heat 1, 2000°F/4 hours, W.Q.		Heat 1, 2000°F/4 hours, W.Q. + 1450°F/24 hours, A.C.		Heat 2, 2000°F/4 hours, W.Q.		Heat 2, 2000°F/4 hours + F.C. 1700°F/24 hours, W.Q.		Heat 2, 2000°F/4 hours, W.Q. + 1450°F/24 hours, A.C.		Published Values References in Parentheses: $Cr_{23}C_6$(68)		Cr_7C_3(68)		Matrix[4]	TiN(18)	
d_{hkl}	I_v[1]	d_{hkl}	I_v	d_{hkl}	I_v	d_{hkl}	I_v	d_{hkl}	I_v	d_{hkl}	I	d_{hkl}	I	d_{hkl}	d_{hkl}	I
2.51	5	2.51	4	2.52	1	2.52	1	2.54	1							
2.46	5	2.46	5	2.45	6	2.46	6	2.45	7						2.44	M
		2.36	1			2.36	-3	2.36	1	2.38	MS					
		2.29	-3			2.29	2	2.29	2			2.30	MW			
2.23	2	2.23	3	2.22	3	2.23	2	2.23	3							
		2.17	1			2.17	-3	2.17	1	2.17	M					
2.12	3	2.12	5	2.12	7	2.12	7	2.12	8			2.12	M		2.12	VS
2.06	6	2.04	4			2.04	3	2.04	5	2.04	S	2.04	VS	2.05		
		1.97	1	1.97	3	1.97	4	1.98	4							
1.91	-3	1.89	1	1.88	-3	1.88	2	1.88	2	1.88	M					
1.86	-3	1.85	-3	1.85	-3	1.85	-3	1.84	1							
1.82	3	1.81	2	1.81	-3	1.81	1	1.81	2			1.81	M			
		1.78	-2	1.77	-3	1.78	-3			1.79	M			1.78		
1.74	-3	1.74	2			1.75	1	1.75	2			1.74	M			
1.68	5	1.67	2	1.65	-2	1.67	-1	1.67	1	1.68	W					
1.60	2	1.60	5	1.60	2	1.60	1	1.60	2	1.60	MW					
1.54	3	1.54	2	1.54	2	1.55	1	1.54	-1							
1.50	3	1.50	2	1.50	5	1.50	5	1.50	7						1.50	S
1.48	5	1.47	2					1.47	-1			1.46	VW			
1.44	2	1.43	1					1.43	-1							
		1.37	2					1.37	1							
1.32	1			1.31	1	1.35	1	1.35	1			1.35	VW			
1.28	1	1.28	2	1.27	3	1.28	3	1.28	6	1.29	M				1.28	M
1.26	1	1.26	2					1.26	-3	1.25	MS			1.26		
1.21	-3	1.22	2	1.22	2	1.23	2	1.23	2	1.23	MS	1.21	M		1.22	VW
		1.19	-3			1.19	2	1.18	2			1.18	M			
		1.17	-3			1.17	2	1.17	2			1.16	M			
1.09	-3	1.06	1	1.06	1	1.06	1	1.06	2	1.08	S			1.07	1.06	VW
1.04	1	1.04	-1	1.02	-3									1.03		
.974	-3	.973	1	.974	2	.971	4	.971	2						.971	M
.949	-2	.948	3	.947	3	.948	3	.946	3						.946	S
.867	-3	.866	3	.866	4	.865	4	.864	4							

Heat 1, 2000°F/4 hours, W.Q. + 1450°F/1000 hours, A.C.		Heat 2, 2000°F/4 hours, W.Q. + 1450°F/15 minutes, A.C.		Heat 2, 2000°F/4 hours, W.Q. + 1450°F/1000 hours A.C.				Heat 3, 2000°F/4 hours, W.Q. + 1450°F/24 hours, A.C.				Heat 4, 2000°F/4 hours, W.Q. + 1450°F/24 hours, A.C.				Published Values References in Parentheses: $Cr_{23}C_6$(68)		Cr_7C_3(68)		Matrix[4]	TiN(18)	
d_{hkl}	I_v	d_{hkl}	I_v	d_{hkl}	I_v	I_i[2]	W[3]	d_{hkl}	I_v	I_i	W	d_{hkl}	I_v	I_i	W	d_{hkl}	I	d_{hkl}	I	d_{hkl}	d_{hkl}	I
2.52	5	2.53	-3	2.52	1			2.55	3			2.54	-3									
2.45	4	2.45	7	2.46	7	4.90	0.75	2.45	7	5.06	0.75	2.45	7	6.00	0.75						2.44	M
2.37	3	2.37	-3	2.37	3	0.69	0.70	2.37	1	0.25	0.65	2.37	-3	--	--	2.38	MS					
2.28	-3	2.28	1	2.29	1	0.16	0.65	2.30	3	0.50	0.65	2.29	1	0.80	0.65			2.30	MW			
2.22	5	2.22	2	2.23	3	0.70	0.70	2.23	3	0.45	0.70	2.23	1	0.55	0.70							
2.16	2			2.17	1	--	--	2.18	1	--	--	2.17	-3	--	--	2.17	M					
2.12	5	2.12	8	2.12	8	4.97	0.70	2.12	8	5.35	0.75	2.12	8	7.08	0.70			2.12	M		2.12	VS
2.04	4	2.04	-3	2.05	5			2.04	4			2.04	3			2.04	S	2.04	VS	2.05		
1.97	1	1.97	3	1.96	-3			1.97	-3			1.97	3									
1.88	-1	1.88	2	1.88	-1			1.88	-3			1.88	1			1.88	M					
								1.85	-3			1.85	1									
1.80	-1	1.82	-3					1.81	2			1.81	1									
				1.79	2											1.79	M			1.78		
1.73	1	1.74	1	1.75	-3			1.74	3			1.75	-2					1.74	M			
1.67	2	1.67	1	1.67	1			1.67	1			1.67	-3			1.68	W					
1.60	4	1.60	1	1.60	2			1.60	4			1.60	-2			1.60	MW					
1.54	4	1.54	-3	1.54	1			1.54	1			1.54	-3									
1.50	4	1.50	7	1.50	5			1.50	5			1.50	7								1.50	S
1.47	3	1.47	-1					1.47	-3			1.46	-3					1.46	VW			
1.42	1							1.43	-3			1.43	-3									
1.38	1							1.37	2													
1.34	-3			1.35	-3			1.34	1									1.35	VW			
1.28	-1	1.28	5	1.28	3			1.28	3			1.28	4			1.29	M				1.28	M
1.26	2	1.26	-3	1.26	1											1.25	MS			1.26		
1.22	2	1.23	4	1.23	3			1.23	2			1.23	3			1.23	MS	1.21	M		1.22	VW
		1.19	1	1.19	1	0.18	0.65	1.19	3	0.46	0.65	1.18	1	0.41	0.70			1.18	M			
		1.17	1	1.17	1	0.26	0.55	1.17	3	0.52	0.65	1.16	1	0.62	0.70			1.16	M			
1.06	1	1.06	2	1.06	1			1.07	1			1.06	1			1.08	S			1.07	1.06	VW
								1.04	1											1.03		
.974	-2	.972	2	.971	3			.974	2			.974	3								.971	M
.943	2	.946	2	.946	2			.948	3			.946	4								.946	S
.868	2	.865	3	.863	3			.865	4			.864	4									

1. Visual intensity classification - 1 through 8 corresponding to usual classification VVW(1) to VS(8). -1 to -3 used to classify extremely weak lines.
2. I_i - Integrated intensity measured from microphotometer traces.
3. Diffraction Line width (2θ°) at 1/2 peak intensity.
4. Calculated on basis of FCC structure with $a_o = 3.56$ Å.

TABLE VIII

X-RAY DIFFRACTION DATA FROM ELECTROLYTIC HYDROCHLORIC ACID EXTRACTS

(All d values in A units; copper radiation)

Heat 1 2000°F/4 hours, W.Q. + 1450°F/24 hours				Heat 1 2000°F/4 hours, W.Q. + 1450°F/24 hours		Heat 2 2000°F/4 hours, W.Q. + 1450°F/24 hours				Heat 2 2000°F/4 hours, W.Q. + 1450°F/24 hours		Published Values References in Parentheses							
												$Cr_{23}C_6$(68)		Cr_7C_3(68)		Matrix[4]	TiN(18)		
d_{hkl}	I_v[1]	I_i[2]	W[3]	d_{hkl}	I_v	d_{hkl}	I_v	I_i	W	d_{hkl}	I_v	d_{hkl}	I	d_{hkl}	I	d_{hkl}	d_{hkl}	I	
2.51	2			2.52	1	2.55	1			2.54	-2								
2.44	2	0.48	0.65	2.45	2	2.45	7	2.31	0.55	2.45	7							2.44	M
2.37	1	0.43	0.45	2.36	1	2.38	1	0.21	0.50	2.37	-1	2.38	MS						
2.28	-3	0.07	0.40	2.29	-3	2.29	3	0.66	0.50	2.29	2			2.30	MW				
2.22	2	0.38	0.50	2.22	3	2.23	-3	--	--	2.23	3								
2.16	1	0.25	0.50	2.17	1	2.17	1	0.16	0.50	2.16	-1	2.17	M						
2.11	3	0.76	0.65	2.12	3	2.11	8	4.23	0.60	2.12	8			2.12	M			2.12	VS
2.05	8	8.60	0.70	2.05	8	2.05	5			2.04	5	2.04	S	2.04	VS	2.05			
1.97	4			1.98	4	1.97	4			1.98	4								
1.93	-3									1.92	-2								
1.88	1			1.89	3	1.88	1			1.88	2	1.88	M						
						1.84	1			1.84	-2								
1.81	-3					1.81	3			1.81	2			1.81	M				
1.78	7			1.78	6							1.79	M			1.78			
1.72	-3			1.72	-3	1.75	1			1.75	2			1.74	M				
1.67	-3			1.67	-3	1.67	1			1.67	1	1.68	W						
1.64	-3			1.64	-3	1.64	-3												
1.60	-2			1.60	1	1.60	1			1.60	1	1.60	MW						
1.54	2			1.54	1	1.54	-3			1.54	-2								
1.50	2			1.50	2	1.50	6			1.50	7							1.50	S
1.46	-3					1.47	-3			1.47	-1			1.46	VW				
1.42	-3			1.42	-3	1.43	-3			1.43	-1								
1.38	-3			1.38	-3	1.37	-3			1.37	-1			1.35	VW				
1.31	1			1.32	-3	1.33	-2			1.35	-2								
1.28	-3			1.28	-3	1.28	4			1.28	6	1.29	M					1.28	M
1.26	6			1.26	5	1.26	1			1.26	2	1.25	MS			1.26			
1.22	-3			1.23	-3	1.23	3			1.22	2	1.23	MS					1.22	VW
1.21	-3			1.21	-3	1.21	2			1.21	3			1.21	M				
1.19	-3	--	--	1.19	-3	1.19	3	0.50	0.80	1.19	2			1.18	M				
1.17	-3	--	--	1.16	-3	1.17	3	0.67	0.80	1.17	2			1.16	M				
1.07	6			1.07	5	1.07	1			1.07	1	1.08	S						
1.06	-3					1.06	1			1.06	1					1.07	1.06	VW	
1.05	-3			1.05	-3	1.04	-3			1.05	-3								
1.03	5			1.03	4	1.03	-2			1.03	-3					1.03			
.974	-3			.975	-2	.973	3			.974	2						.971	M	
.948	-3			.949	-3	.948	4			.948	4						.946	S	
.866	-2			.865	-2	.866	4			.865	3								

TABLE VIII (Concluded)

Heat 2 2000°F/4 hours, W. Q.		Heat 2 2000°F/4 hours, F.C. to 1700°F/24 hours, W. Q.				Published Values References in Parentheses							
						$Cr_{23}C_6$(68)		Cr_7C_3(68)		Matrix[4]	TiN(18)		
d_{hkl}	I_v	d_{hkl}	I_v	I_i	W	d_{hkl}	I	d_{hkl}	I	d_{hkl}	d_{hkl}	I	
2.53	-3	2.54	-3										
2.45	6	2.44	4	1.55	0.40						2.44	M	
		2.37	-3	--	--	2.38	MS						
		2.29	3	0.55	0.40			2.30	MW				
2.22	3	2.22	-3	--	--								
		2.17	-3	--	--	2.17	M						
2.12	7	2.11	7	3.04	0.38			2.12	M		2.12	VS	
2.05	5	2.04	5			2.04	S	2.04	VS	2.05			
1.97	-3	1.96	1										
1.92	-3	1.90	1										
1.87	-3					1.88	M						
1.84	-3	1.84	2										
		1.81	3					1.81	M				
1.77	3	1.78	-3			1.79	M			1.78			
1.74	-2							1.74	M				
1.67	3	1.67	3			1.68	W						
1.60	3	1.60	2			1.60	MW						
		1.54	1										
1.50	6	1.50	1								1.50	S	
1.47	-3	1.47	6					1.46	VW				
1.43	-3	1.43	-3										
1.37	-2	1.37	-3					1.35	VW				
1.30	-3	1.30	-3										
1.28	4	1.27	5			1.29	M				1.28	M	
		1.26	1			1.25	MS			1.26			
1.22	3	1.22	4			1.23	MS				1.22	VW	
		1.21	3					1.21	M				
		1.19	3	.52	0.40			1.18	M				
		1.17	3	.79	0.60			1.16	M				
1.07	1	1.07	-3			1.08	S						
1.06	1	1.06	3							1.07	1.06	VW	
1.04	-3	1.04	-3										
1.03	-3	1.02	1							1.03			
.973	1	.974	3								.971	M	
.949	4	.949	5								.946	S	
.866	4	.866	5										

1. Visual intensity classification - 1 through 8 corresponding to usual classification VVW(1) to VS(8). -1 to -3 used to classify extremely weak lines.
2. I_i - Integrated intensity measured from microphotometer traces.
3. Diffraction Line width (2θ°) at 1/2 peak intensity.
4. Calculated on basis of FCC structure with a_o = 3.56 A .

TABLE IX

COMPARATIVE DATA FOR THE PRECIPITATION OF γ' DURING AGING AT 1350°, 1400° AND 1450°F

(Initial Condition - Solution Treated 4 hours at 2000°F, W. Q.)

Time at 1350°F (hours)	Heat 1 γ' density[1]	Heat 2 γ' density	Heat 3 γ' density	Heat 4 γ' density
100	478	700	610	650
500	152	183	192	187
1000	100	121	115	111
Time at 1400°F (hours)				
24	510	850[3]	---	---
100	190	315	356	295
250	112	200	182	166
500	71	106	115	100
Time at 1450°F (hours)				
24	185	390	410	405
100	65	129	110	123
500	29	34	37	35
1000	18	24	22	20

Measures of γ' Size and Spacing

Condition: Aged	Heat 1		Heat 2		Heat 3		Heat 4	
	Size[2] (inch)	Spacing (microns)	Size (inch)	Spacing (microns)	Size (inch)	Spacing (microns)	Size (inch)	Spacing (microns)
24 hours at 1400°F	0.017	0.040	0.017[3]	0.026[4]	-----	-----	-----	-----
24 hours at 1450°F	0.026	0.073	0.026	0.036	0.025	0.037	0.026	0.036

1. Number of γ' particles per square inch at 18,000X.
2. Average size of γ' particle at 18,000X, inch.
3. Extrapolated value.
4. Based on extrapolated data.

TABLE X

HARDNESS AND LATTICE PARAMETER OF SPECIMENS AGED AT 1450°F

(Initial Condition - 4 hours at 2000°F, W. Q.)

Time (hours)	Heat 1		Heat 2		Heat 3		Heat 4	
	Hardness (R_B)	Lattice[1] Parameter (Å)	Hardness (R_B)	Lattice Parameter (A)	Hardness (R_B)	Lattice Parameter (Å)	Hardness (R_B)	Lattice Parameter (Å)
0	65.5	3.5623	68.6	3.5638	68.8	3.5643	68.5	3.5656
.25	86.5	3.5617	93.0	3.5638	92.0	3.5642	91.3	3.5658
1	90.4	3.5602	95.8	3.5631	96.0	3.5640	94.2	3.5647
6	92.3	3.5600	98.9	3.5630	98.0	3.5629	96.2	3.5639
24	93.6	3.5602	99.0	3.5630	98.7	3.5625	97.7	3.5628
100	93.0	3.5599	97.5	3.5625	98.9	3.5619	97.1	3.5622
500	91.0	3.5596	97.7	3.5605	96.9	3.5605	96.0	3.5615
1000	89.6	3.5595	96.5	3.5596	96.2	3.5600	95.8	3.5618

1. Lattice Parameter of the matrix.

TABLE XI

CREEP-RUPTURE DATA AT 1350°F AND 28,000 PSI
FOR SPECIAL HEAT TREATMENTS

Creep-Rupture Properties	Heated 4 hours at 2000°F, transfer to 1700°F, held 24 hours, W. Q. + 24 hours at 1450°F, A. C.		Heated 4 hours at 2000°F, W. Q. + 1000 hours at 1450°F, A. C. + 4 hours at 1700°F, W. Q. + 24 hours at 1450°F, A. C.	
	Heat 2	Heat 3	Heat 2	Heat 4
Rupture Life, hours	506.0	720.1	306.3	563.6
Creep Rate x 10^{-5} in./in/hr	0.970	0.740	1.43	1.20
Elongation, percent	2.4	1.6	3.2	4.9
Reduction of Area, percent	2.4	3.1	3.2	6.2

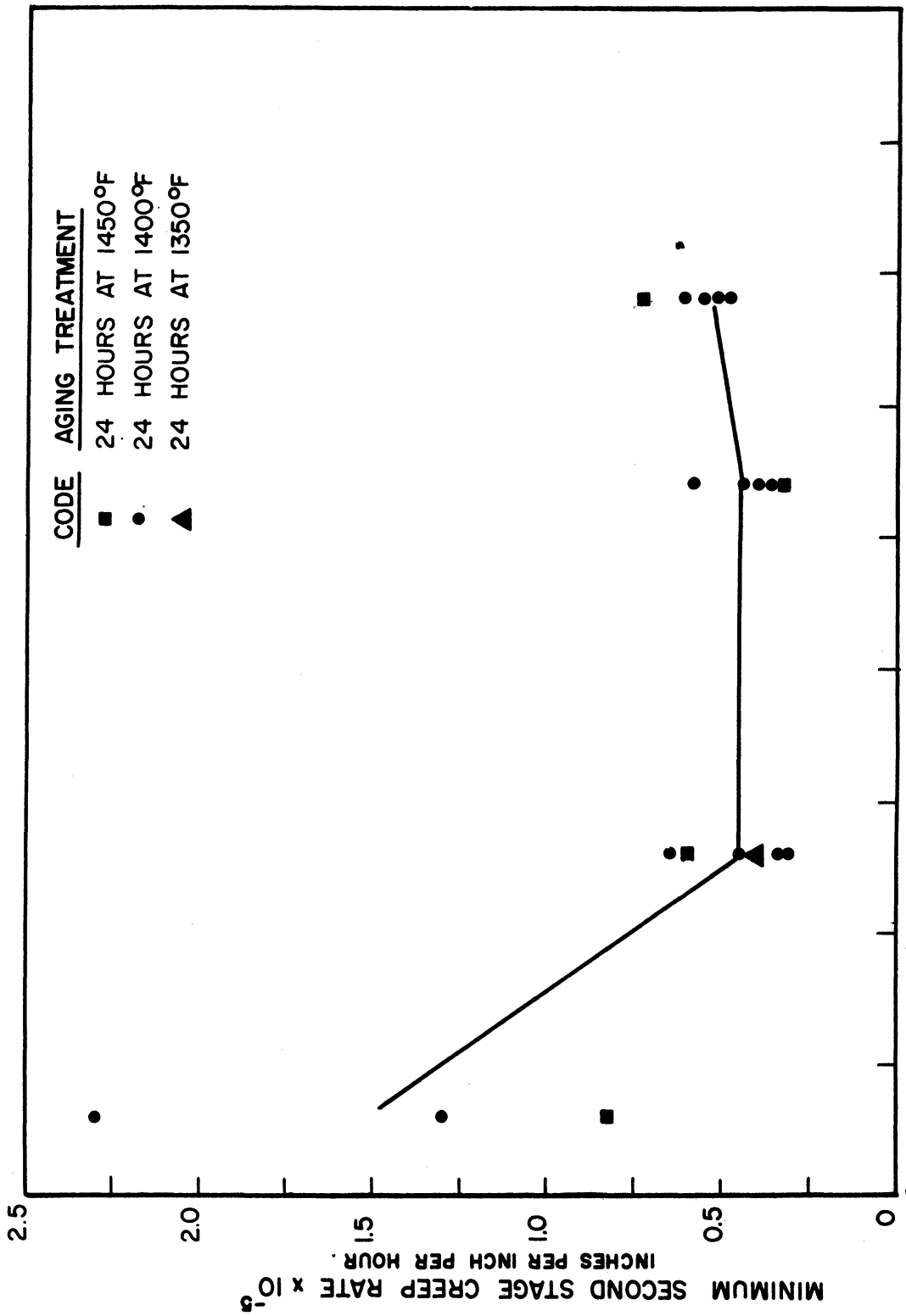


Figure 1. Effect of nitrogen on minimum secondary creep rate at 1350°F and 28,000 psi. Heat treatment prior to testing was 4 hours at 2000°F, W. Q. plus aged as shown.

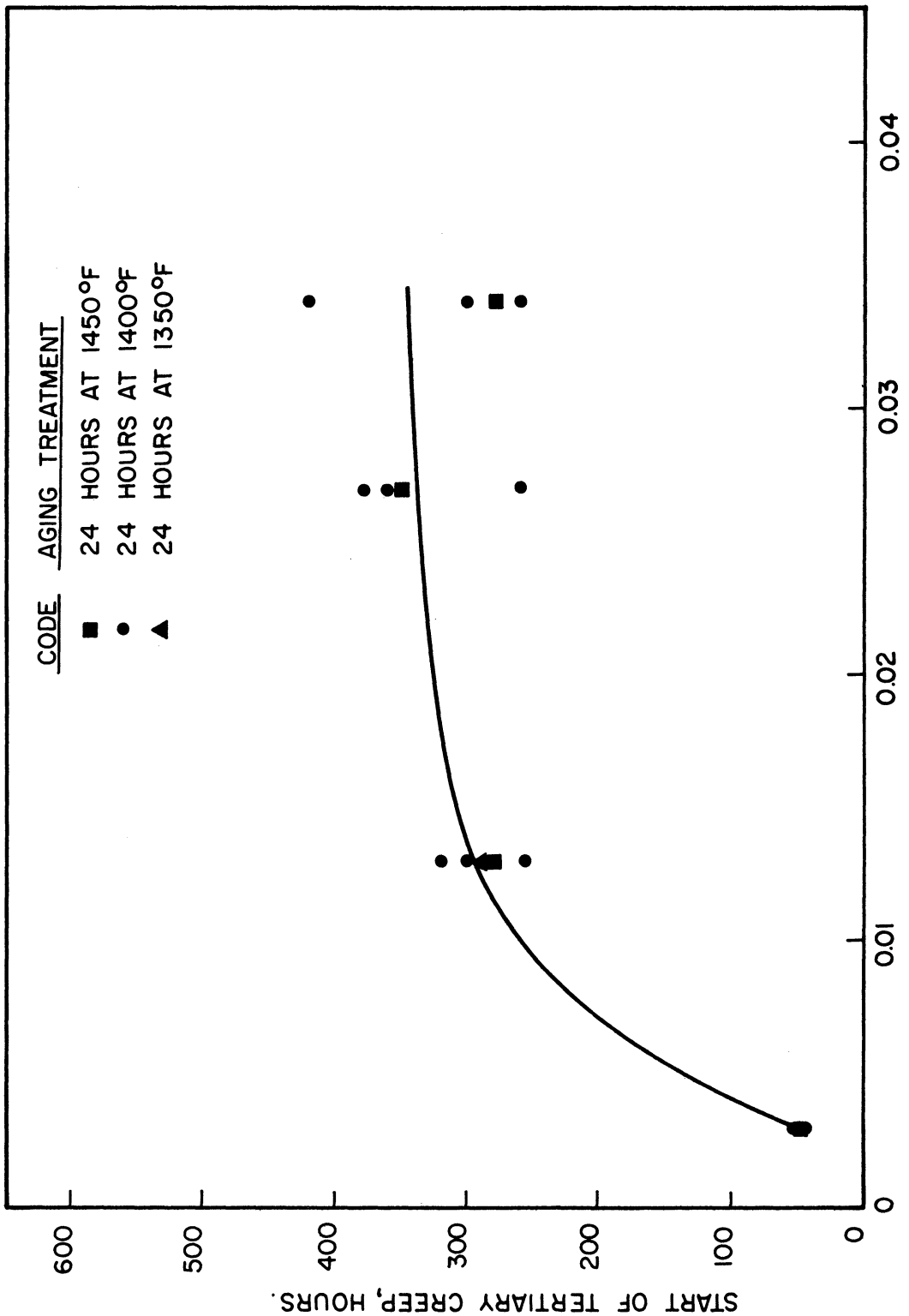


Figure 2. Effect of nitrogen on start of tertiary creep at 1350°F and 28,000 psi. Heat treatment prior to testing was 4 hours at 2000°F, W. Q. plus aged as shown.

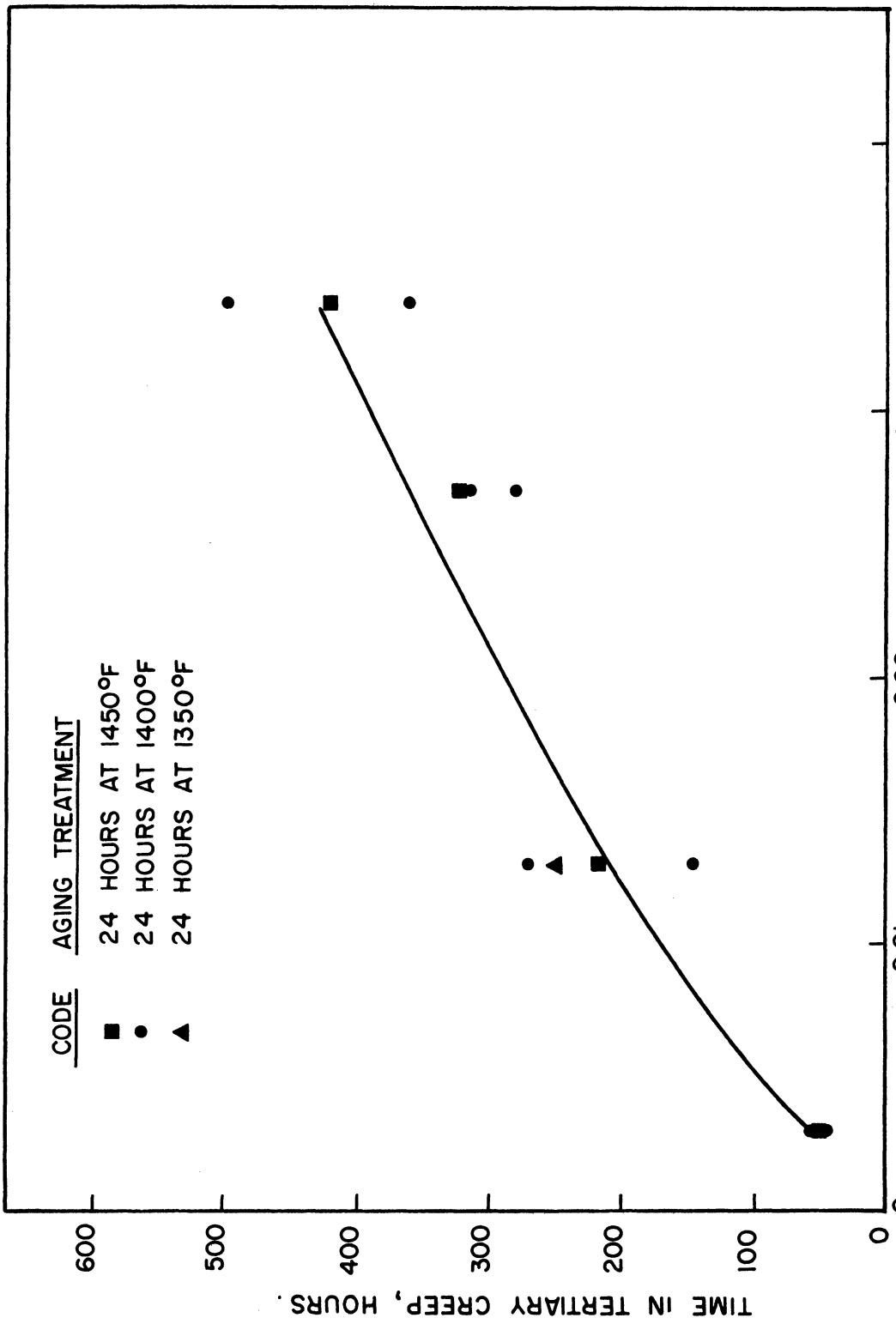


Figure 3. Effect of nitrogen on the time in tertiary creep at 1350°F and 28,000 psi. Heat treatment prior to testing was 4 hours at 2000°F, W. Q. plus ages as shown.

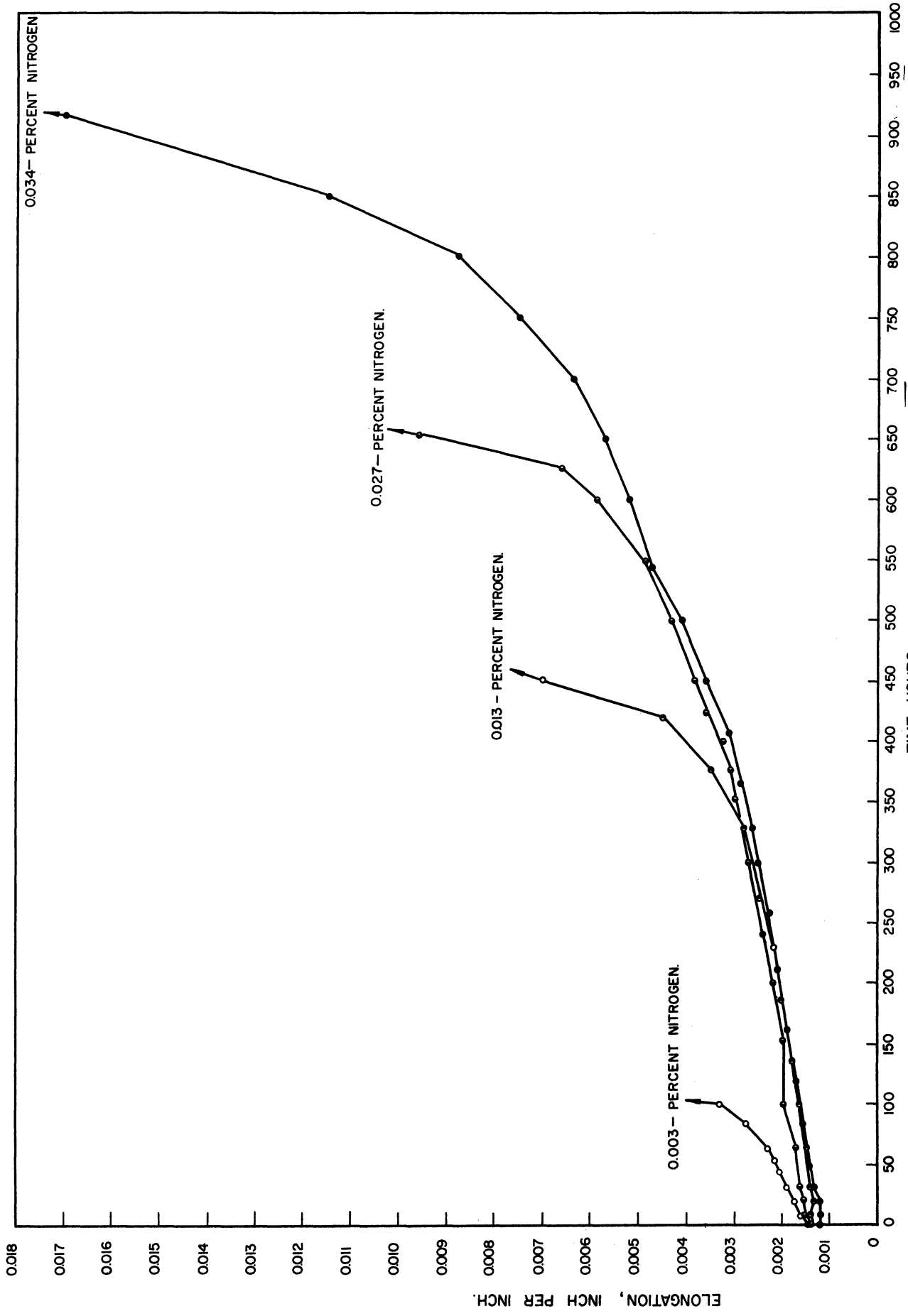


Figure 4. Comparative creep curves at 1350°F and 28,000 psi. Heat treatment prior to testing was 4 hours at 2000°F, W. Q. plus 24 hours at 1400°F.

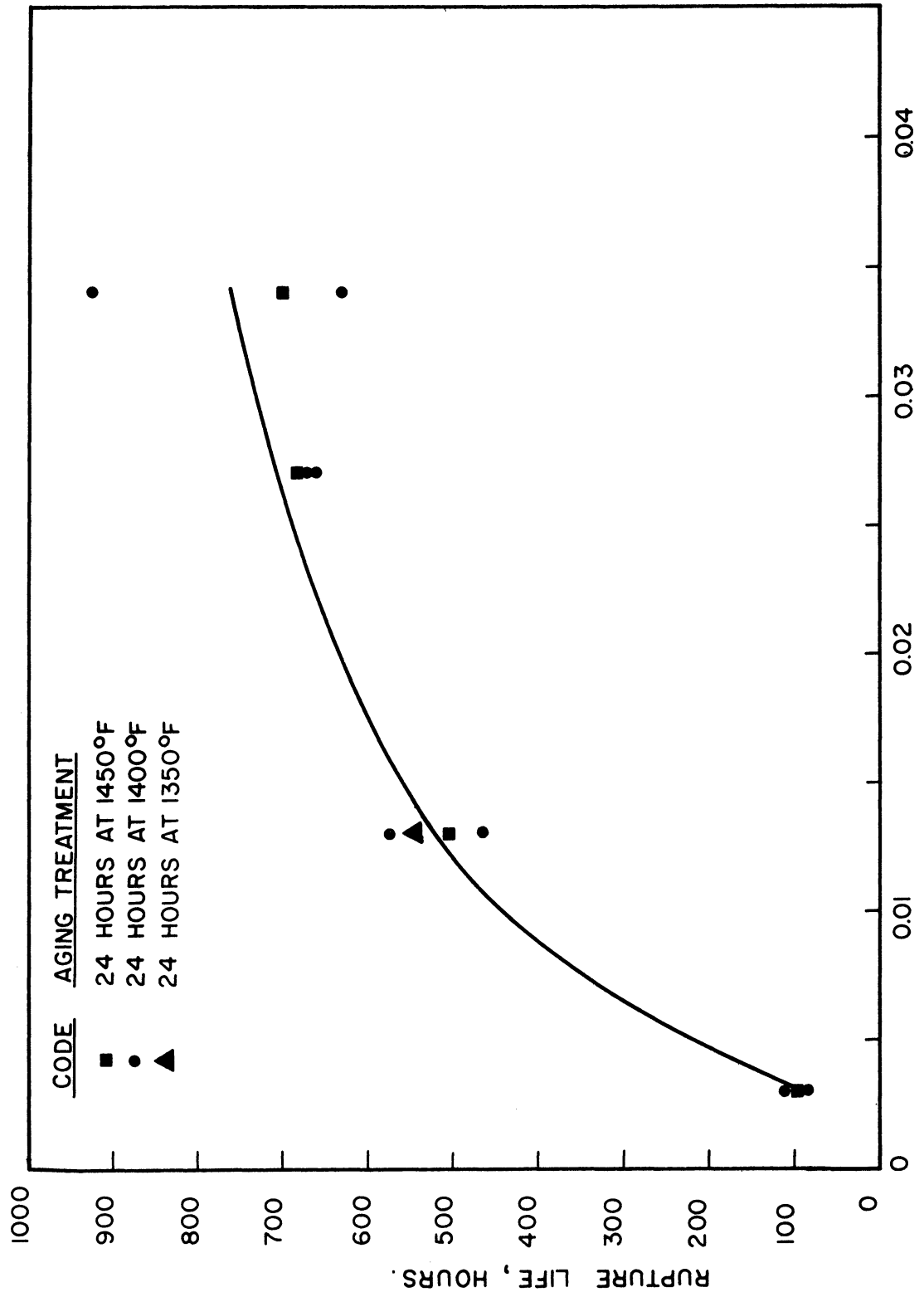


Figure 5. Effect of nitrogen on rupture life at 1350°F and 28,000 psi Heat treatment prior to testing was 4 hours at 2000°F, W. Q. plus aged as shown.

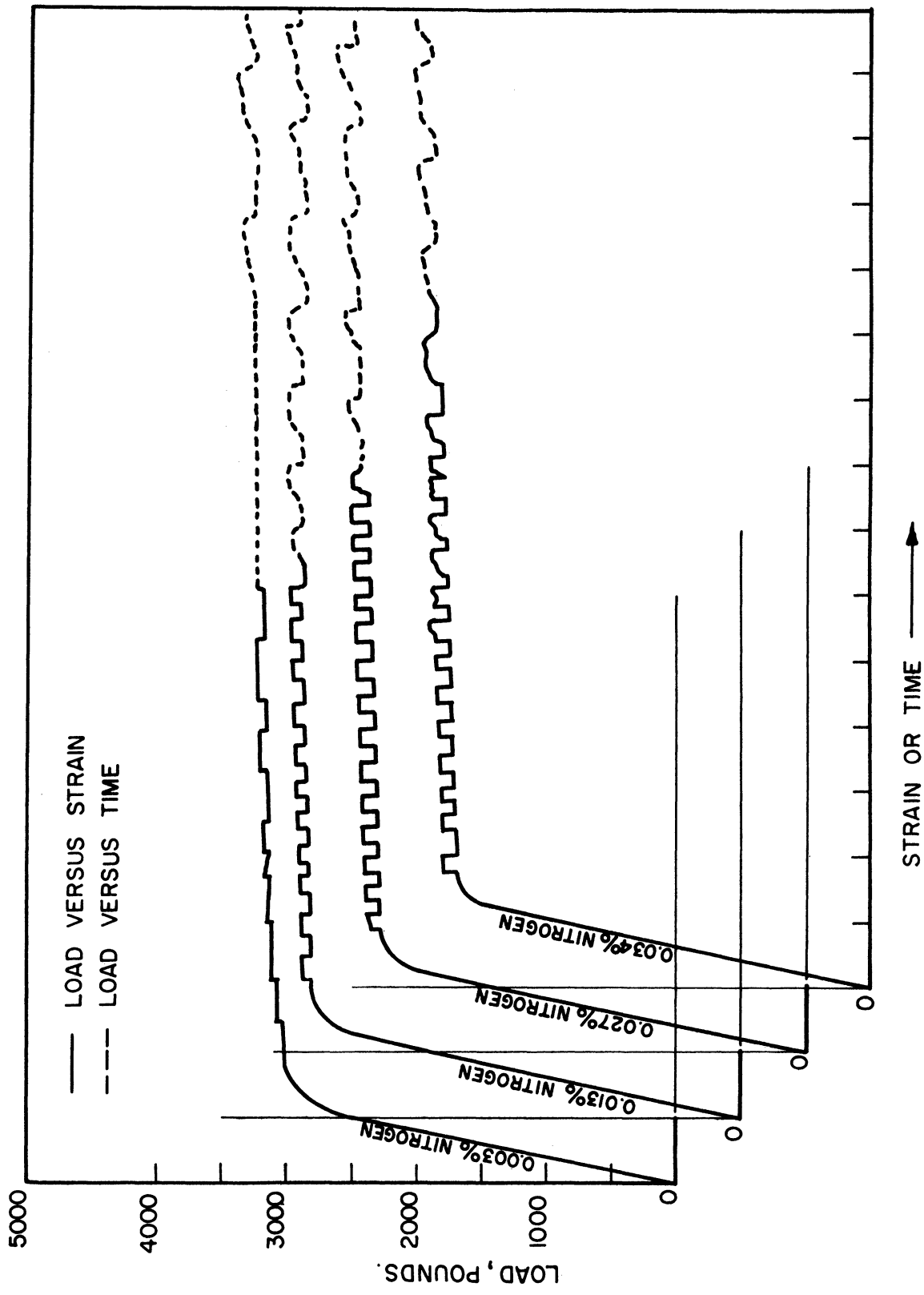
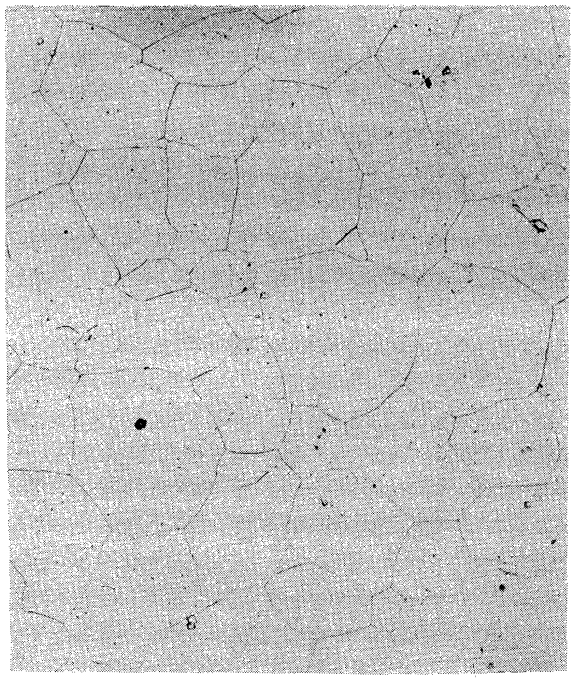
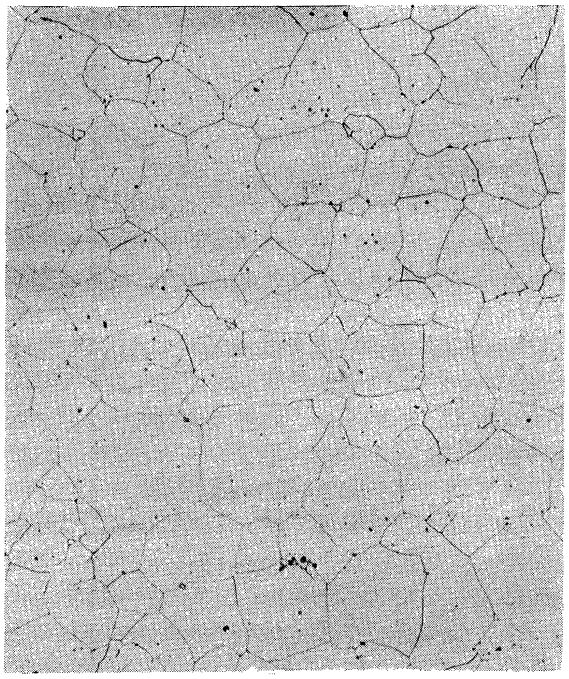


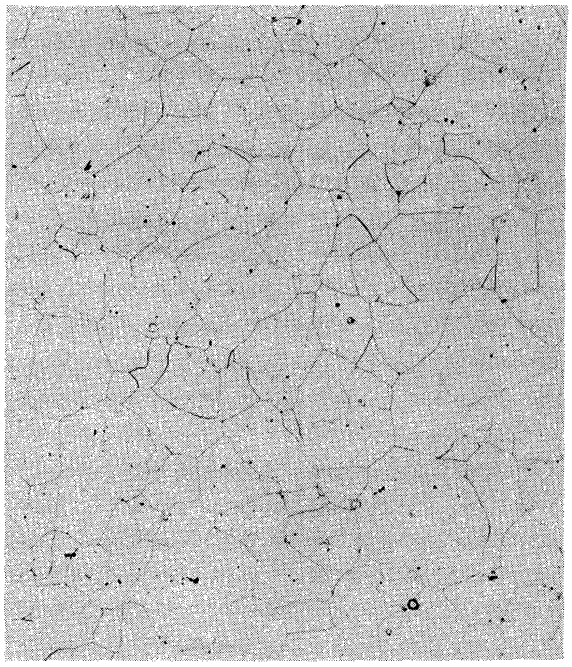
Figure 6. Schematic representation of the effect of nitrogen on the load - strain curves at 900°F. Heat treatment prior to testing was 4 hours at 2000°F, W. Q. plus 24 hours at 1400°F.



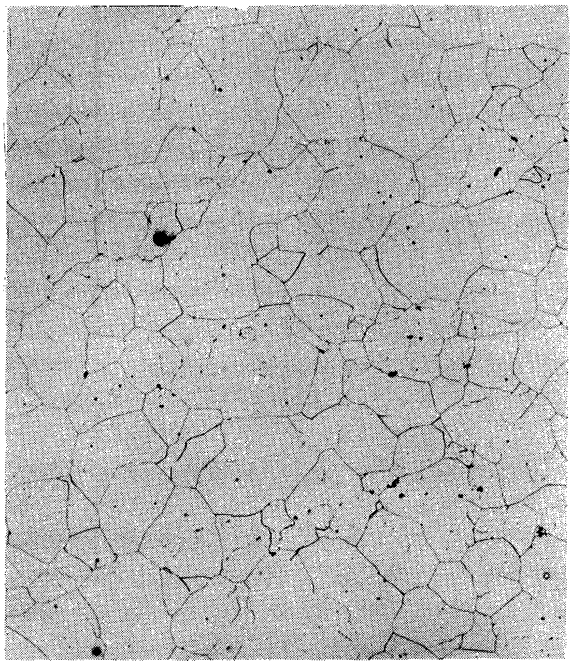
Heat 1 - 0.003-percent nitrogen
65.5 R_B



Heat 2 - 0.013-percent nitrogen
68.6 R_B

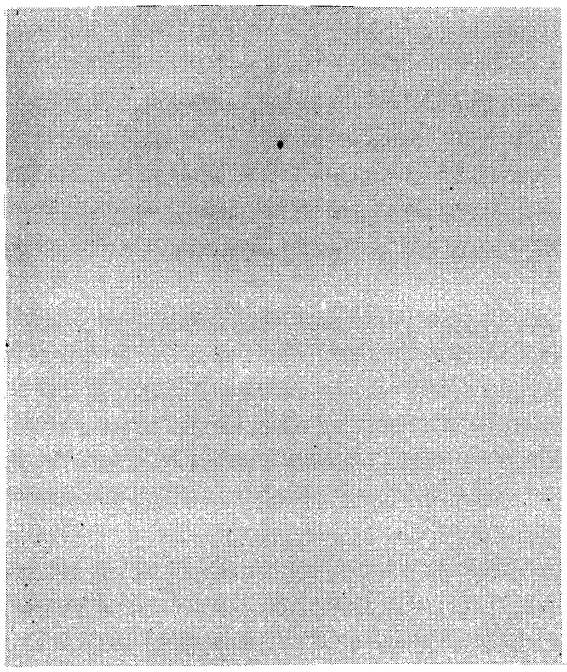


Heat 3 - 0.027-percent nitrogen
68.8 R_B

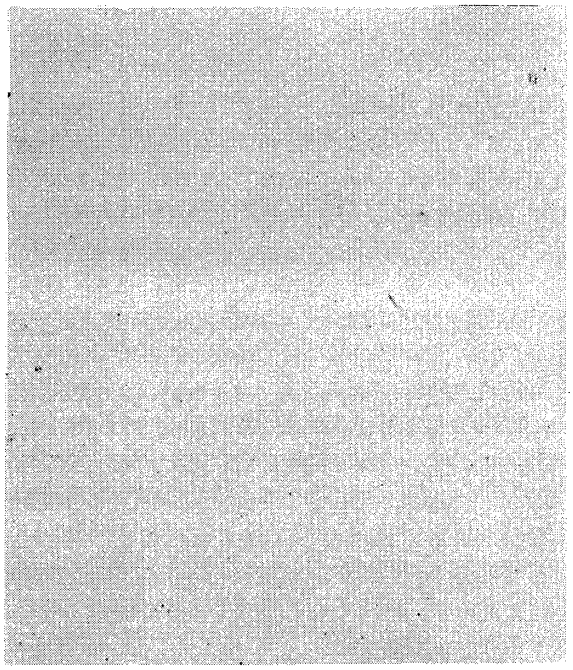


Heat 4 - 0.034-percent nitrogen
68.5 R_B

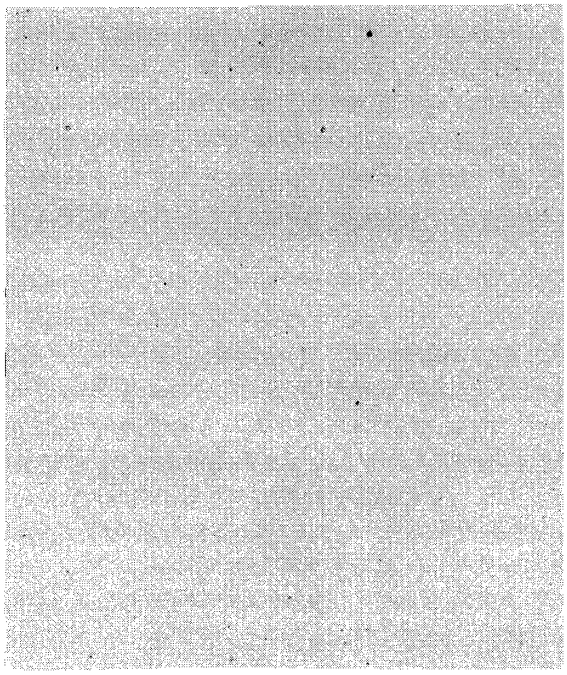
Figure 7. - Microstructures of experimental heats after 4 hours at 2000°F, W. Q. Oxalic acid etch. X100 .



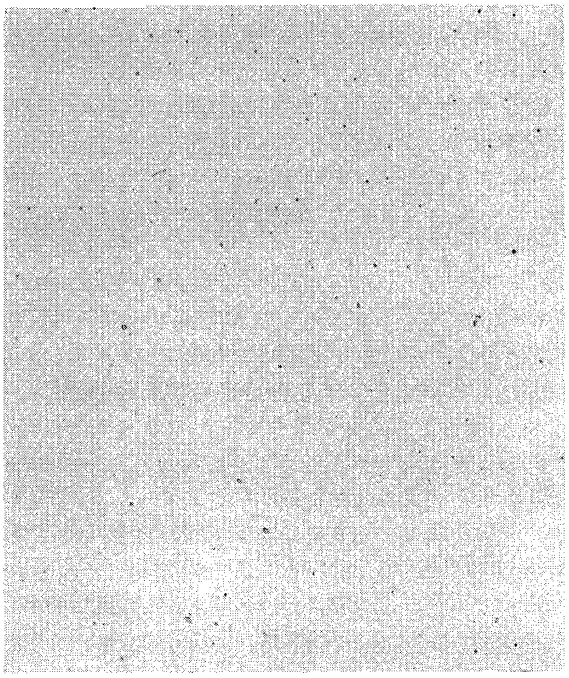
Heat 1 - 0.003-percent nitrogen



Heat 2 - 0.013-percent nitrogen

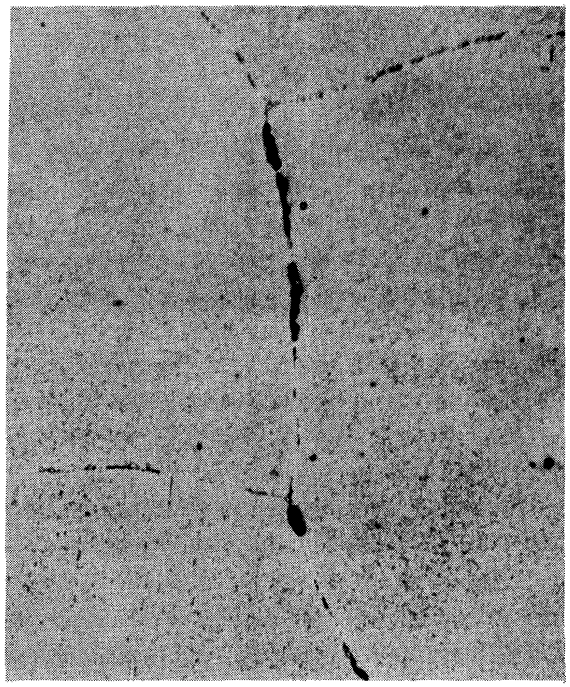


Heat 3 - 0.027-percent nitrogen

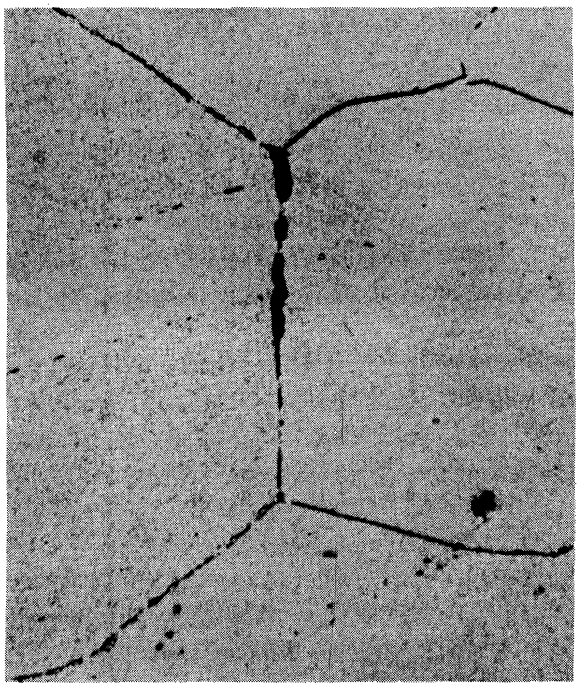


Heat 4 - 0.034-percent nitrogen

Figure 8. - Microstructure of experimental heats after 4 hours at 2000°F, W. Q. Unetched. X100.



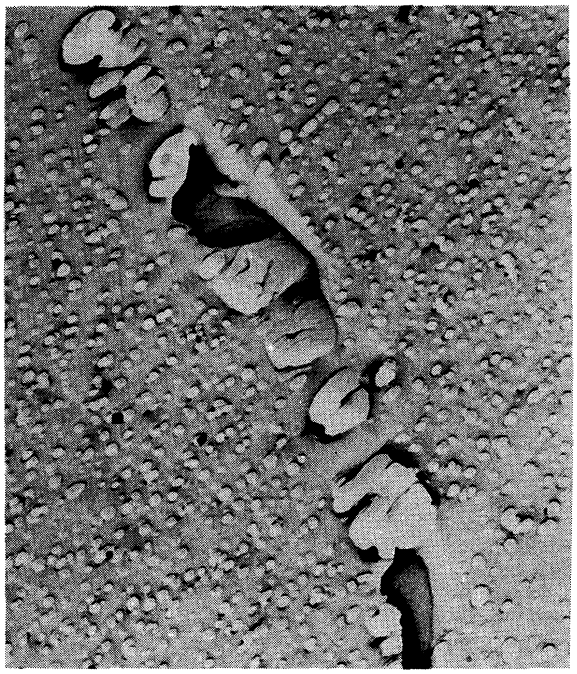
X1000



X1000



X18,000



X18,000

Heat 1 - 0.003-percent nitrogen

Heat 2 - 0.013-percent nitrogen

Figure 9. - Micro-cracks in ruptured specimens of experimental heats 1 and 2. Tension axis is horizontal.

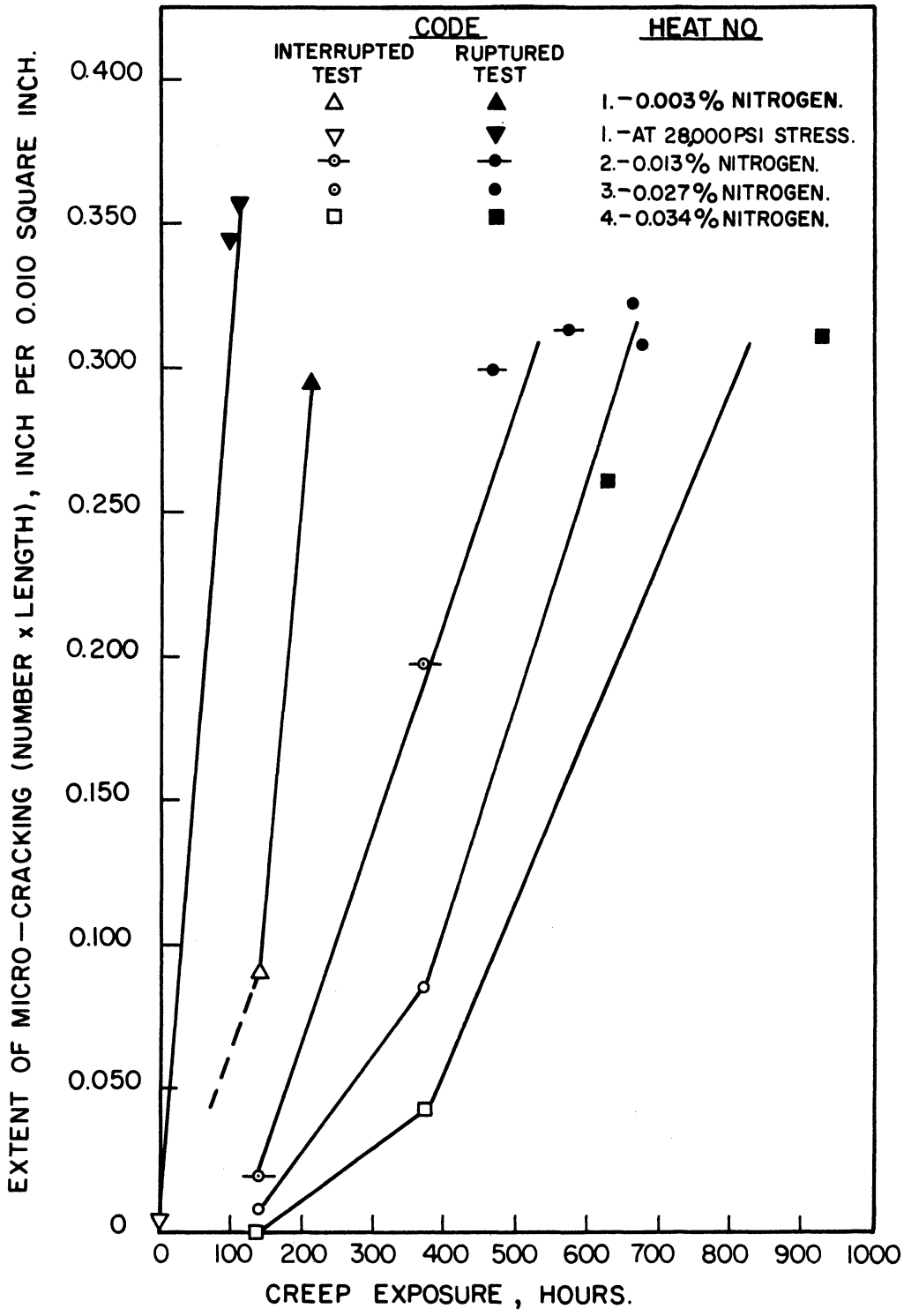


Figure 10. Effect of nitrogen on extent of micro-cracking during creep at 1350°F. Specimens stressed to cause equal rates of creep strain (0.4×10^{-5} in/in/hr) except for 28,000 psi rupture tests on Heat 1 which were at a higher strain rate (1.5×10^{-5} in/in/hr). Heated 4 hours at 2000°F, W. Q. plus 24 hours at 1400°F prior to creep exposure.

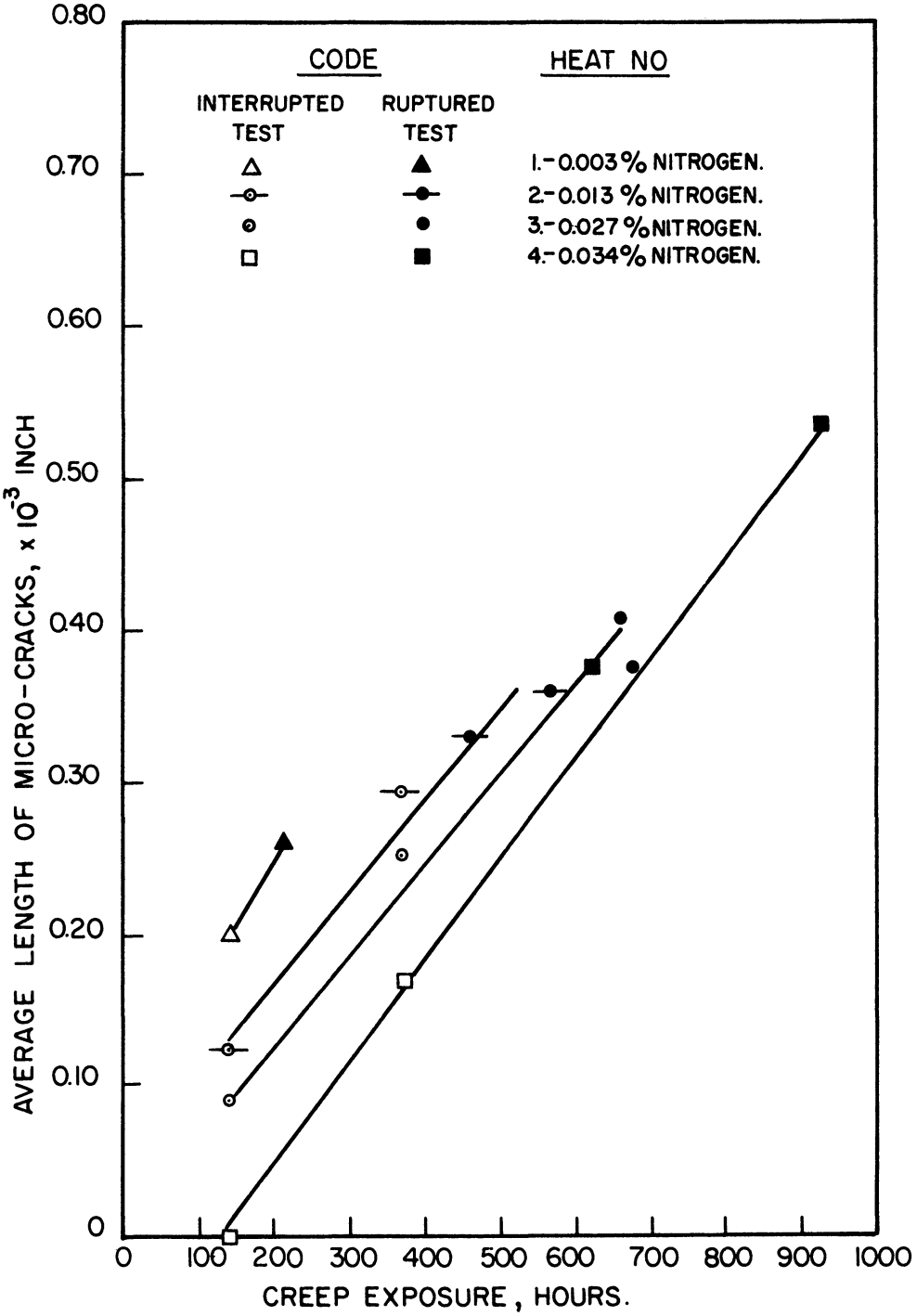


Figure 11. Effect of nitrogen on growth of micro-cracks during creep at 1350°F. Specimens stressed to cause equal rates of strain. Heated 4 hours at 2000°F, W. Q. plus 24 hours at 1400°F prior to creep exposure.

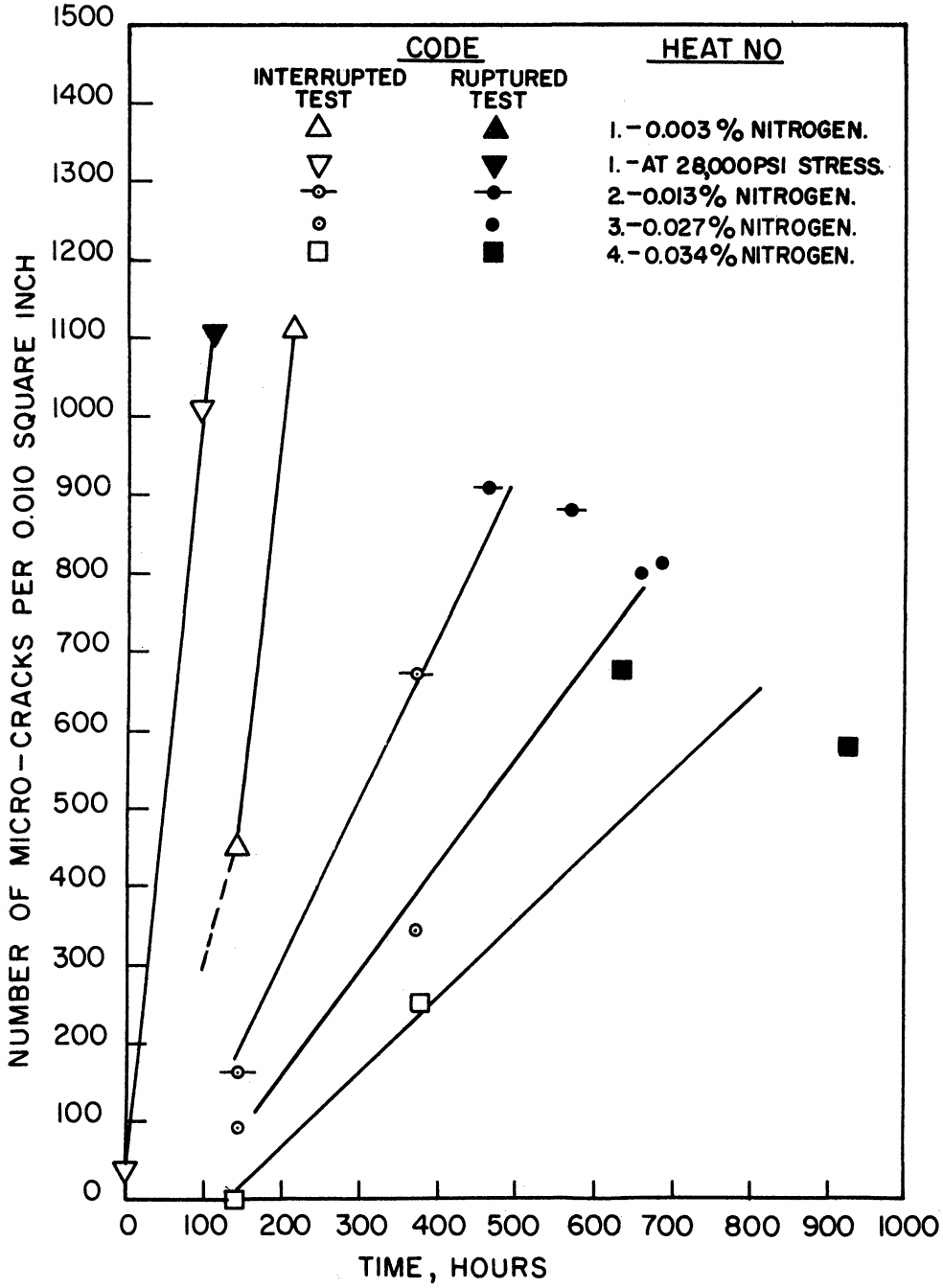


Figure 12. Effect of nitrogen on the number of micro-cracks formed during creep at 1350°F. Specimens stressed to cause equal rates of creep strain (0.4×10^{-5} in/in/hr) except for 28,000 psi rupture tests on Heat 1 which were at a higher strain rate (1.5×10^{-5} in/in/hr). Heated 4 hours at 2000°F, W. Q. plus 24 hours at 1400°F prior to creep exposure.

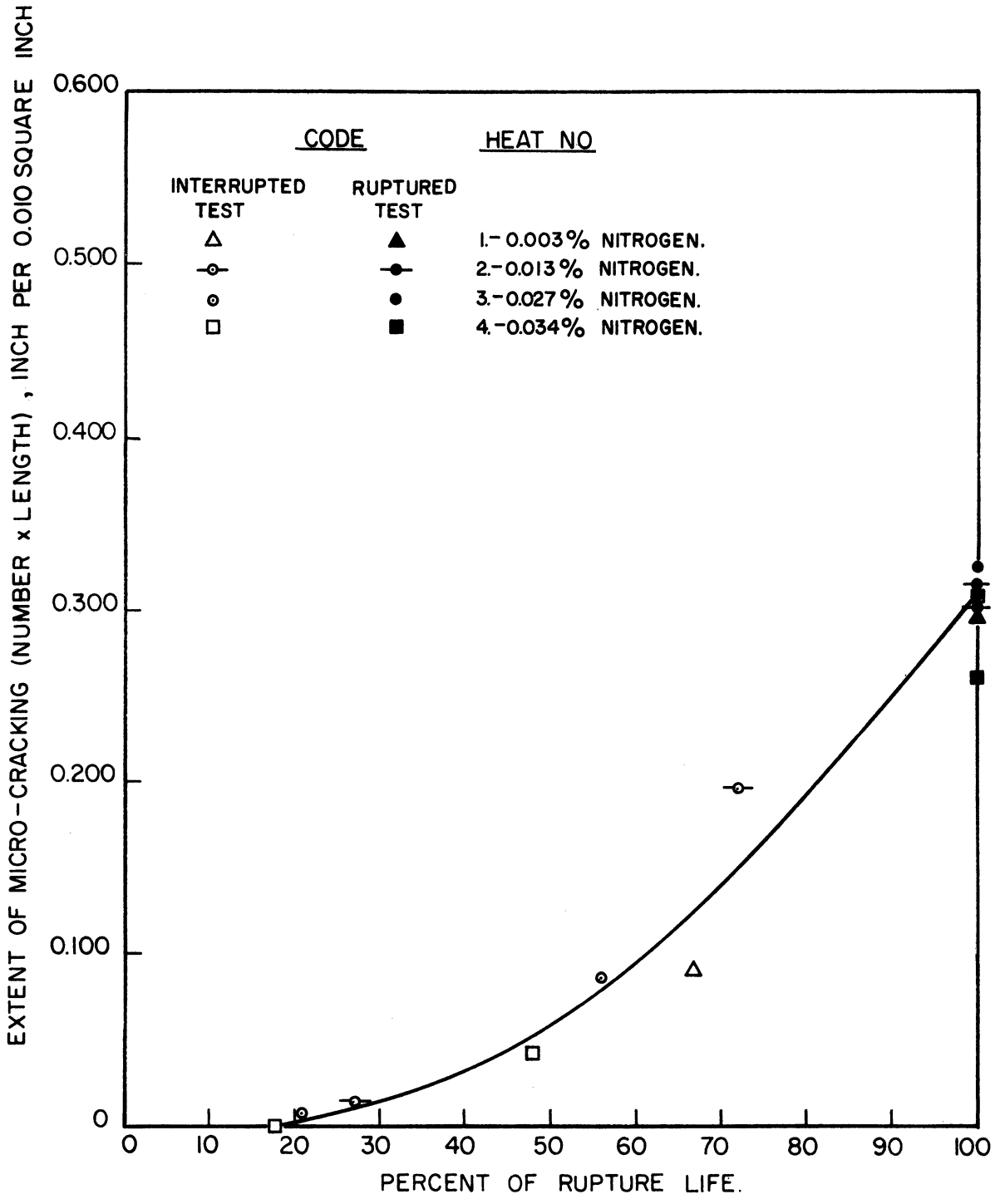
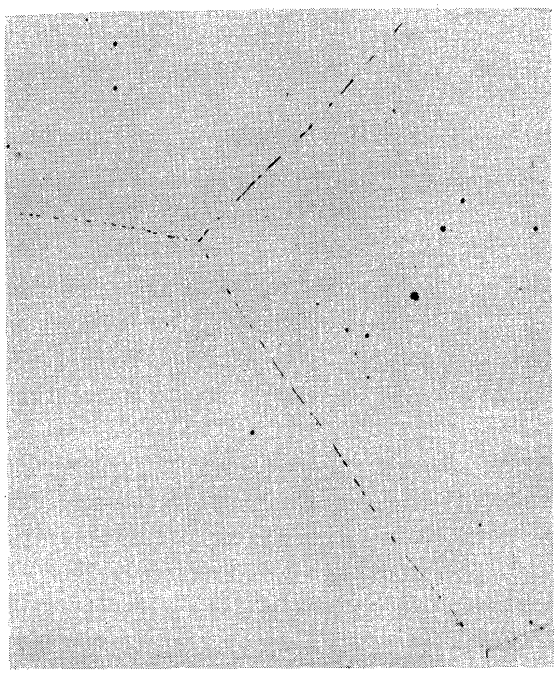
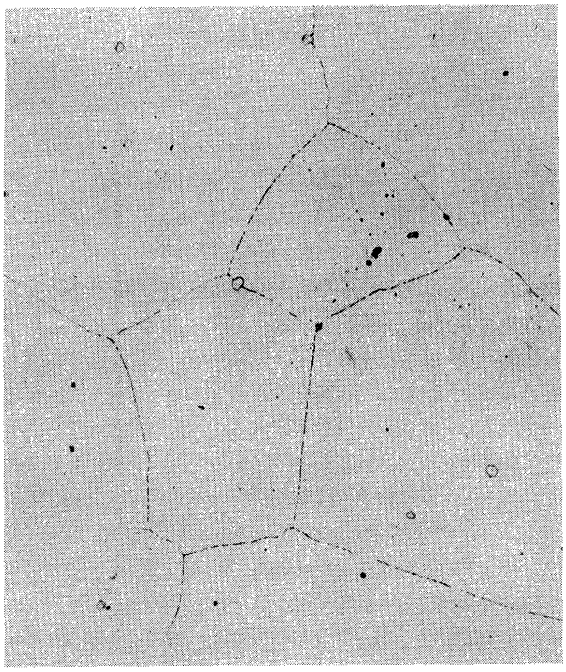


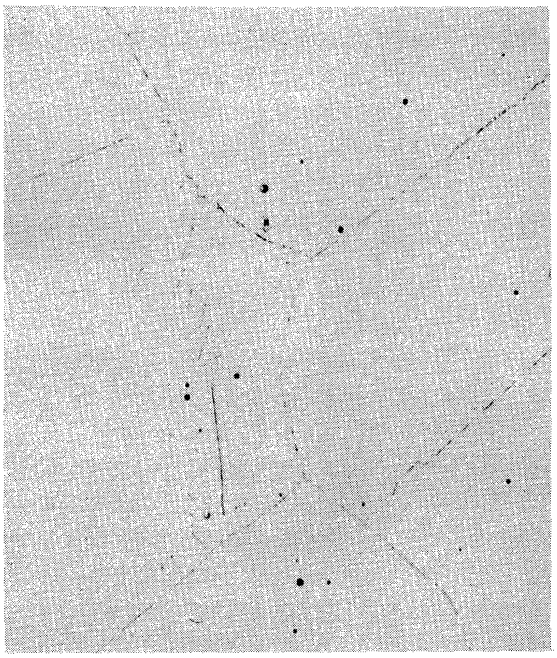
Figure 13. Relation of percent rupture life at 1350°F to the extent of micro-cracking for varying nitrogen heats. Specimens stressed to cause equal rate of creep strain. Heated 4 hours at 2000°F, W. Q. plus 24 hours at 1400°F prior to creep exposure.



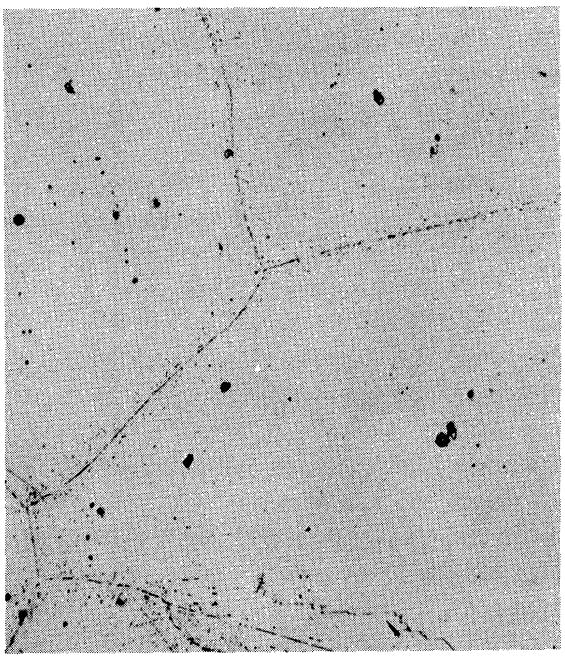
Aged 24 hours



Aged 24 hours



Aged 1000 hours

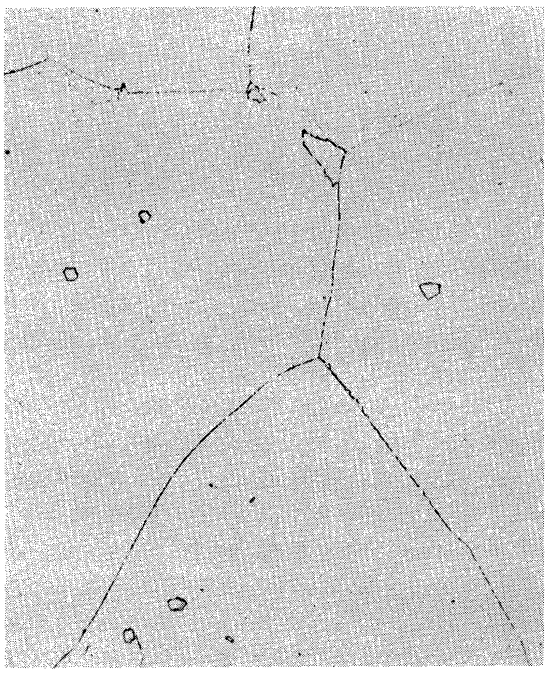


Aged 1000 hours

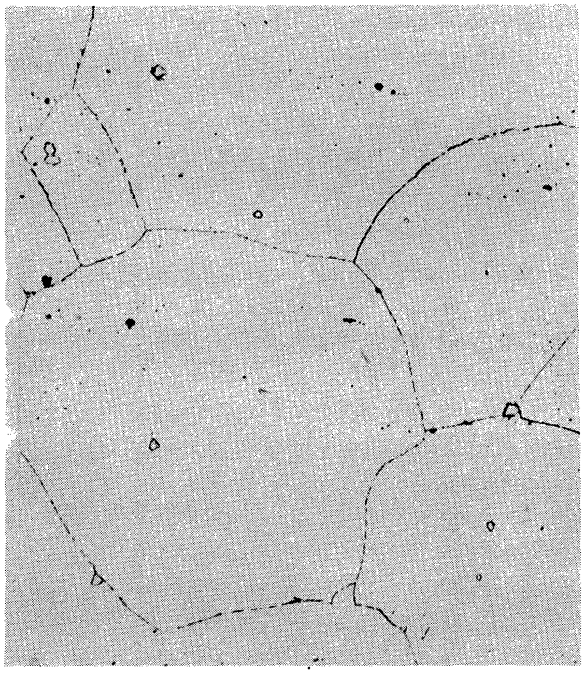
Heat 1 - 0.003-percent nitrogen

Heat 2 - 0.013-percent nitrogen

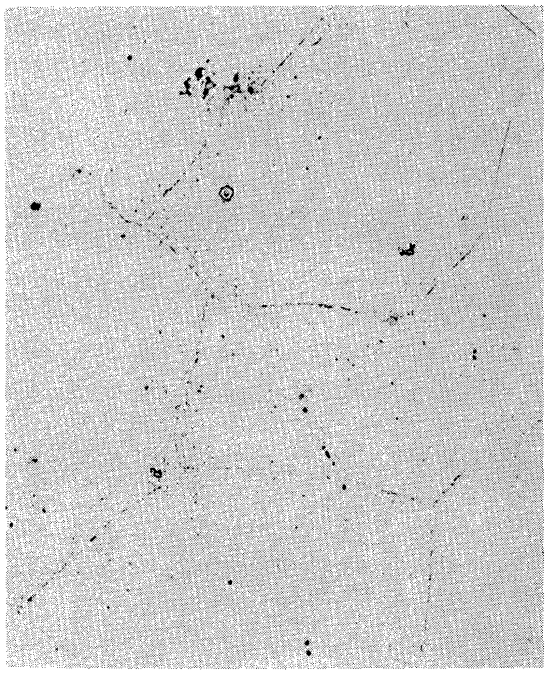
Figure 14. - Effect of aging time at 1350°F on the microstructure of the experimental heats. Heated 4 hours at 2000°F, W. Q. prior to aging. X500.



Aged 24 hours

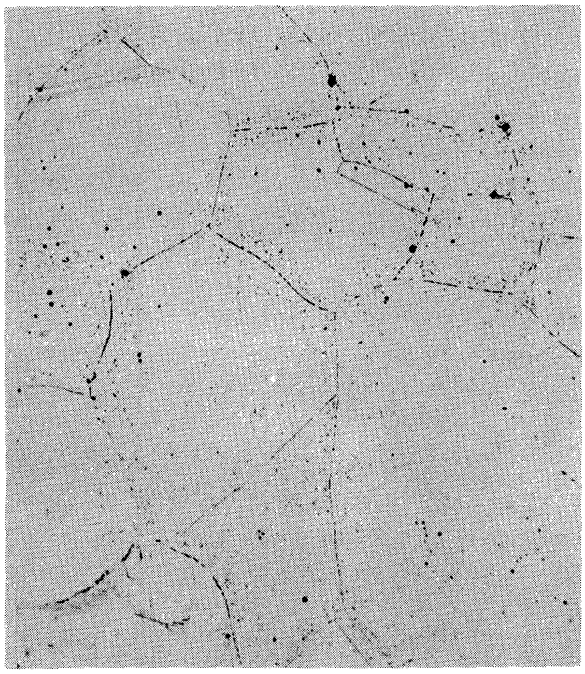


Aged 24 hours



Aged 1000 hours

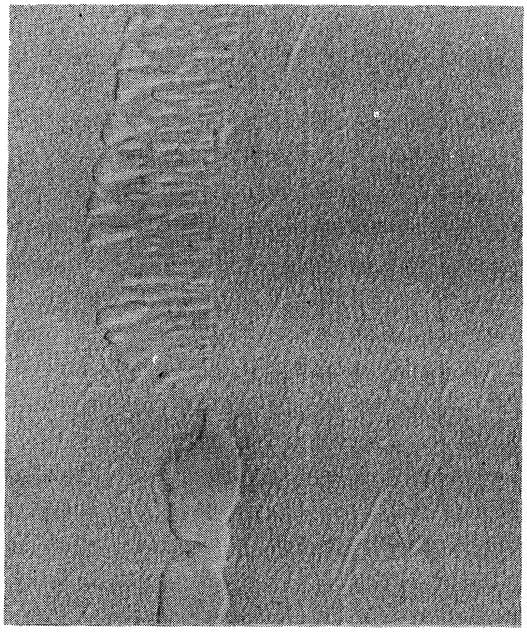
Heat 3 - 0.027-percent nitrogen



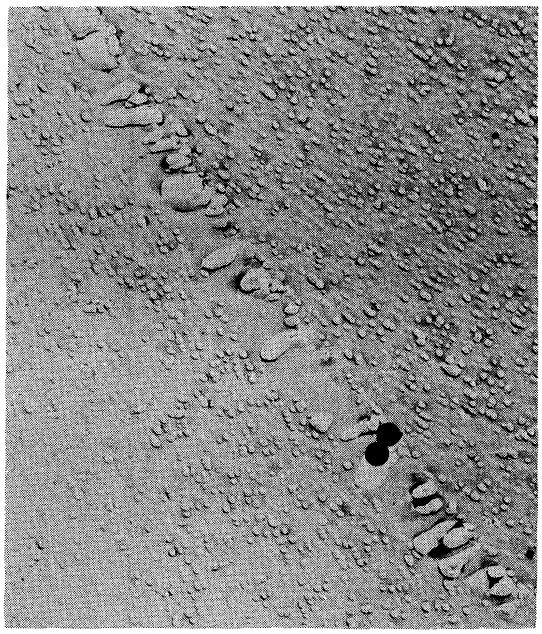
Aged 1000 hours

Heat 4 - 0.034-percent nitrogen

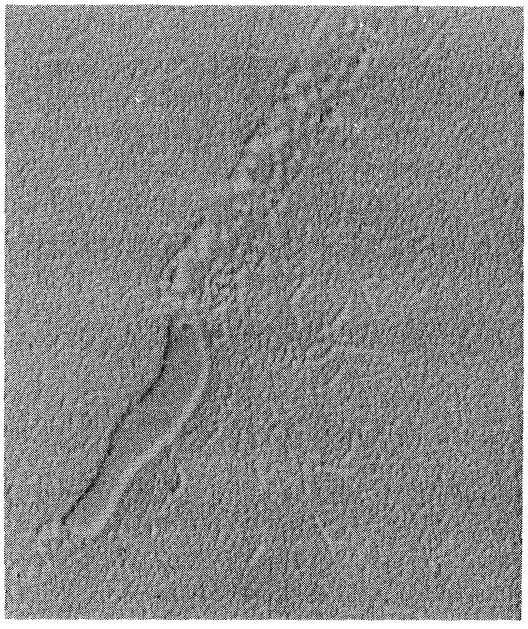
Figure 14. - Concluded.



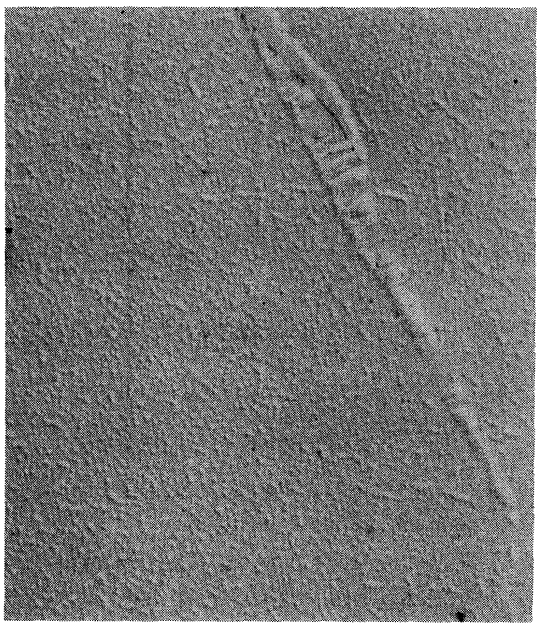
Heat 1 - 0.003-percent nitrogen



Heat 2 - 0.013-percent nitrogen



Heat 3 - 0.027-percent nitrogen



Heat 4 - 0.034-percent nitrogen

Figure 15. - Electron micrographs of typical intergranular cellular precipitates in the experimental heats. X12,000.

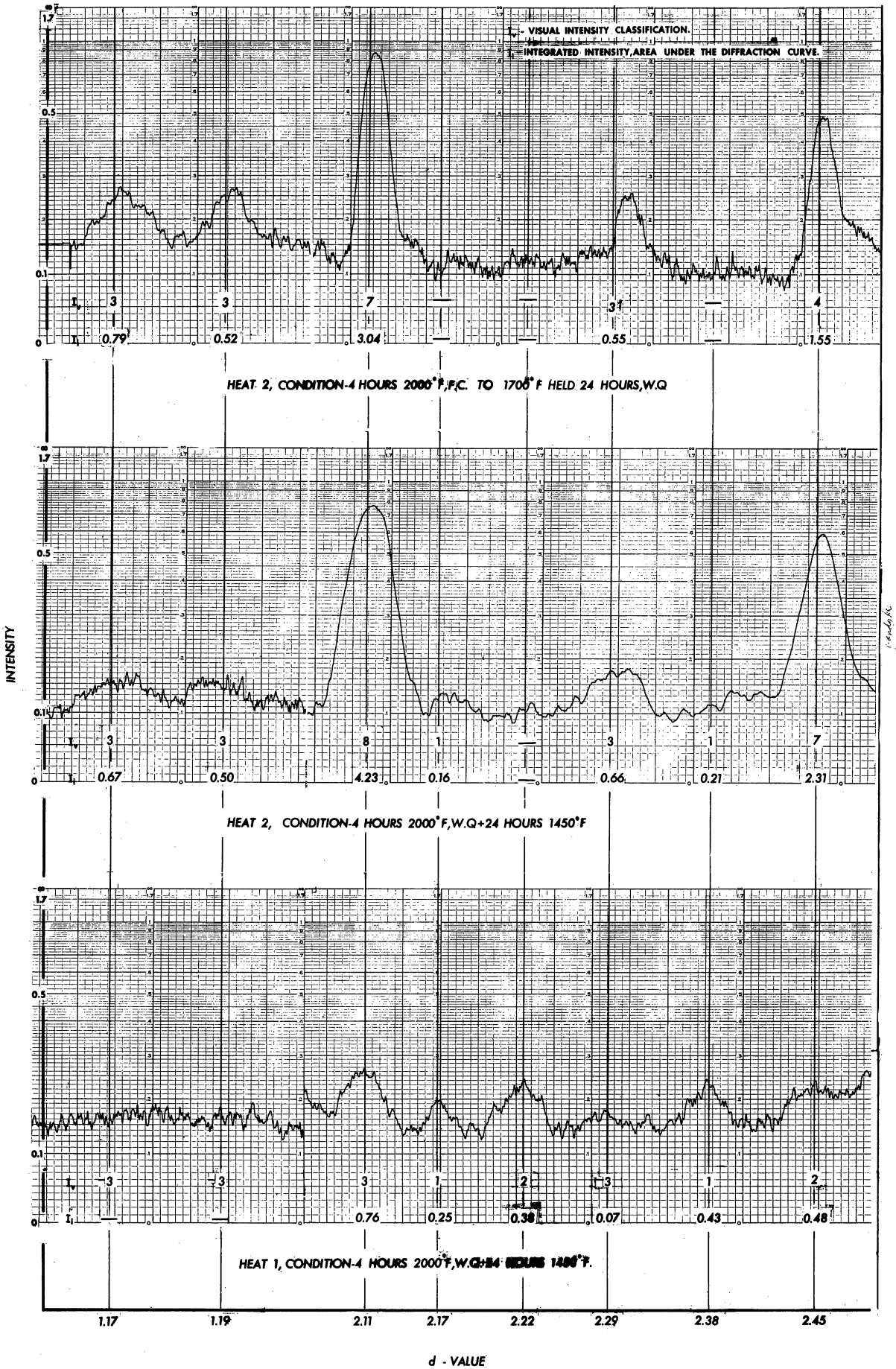
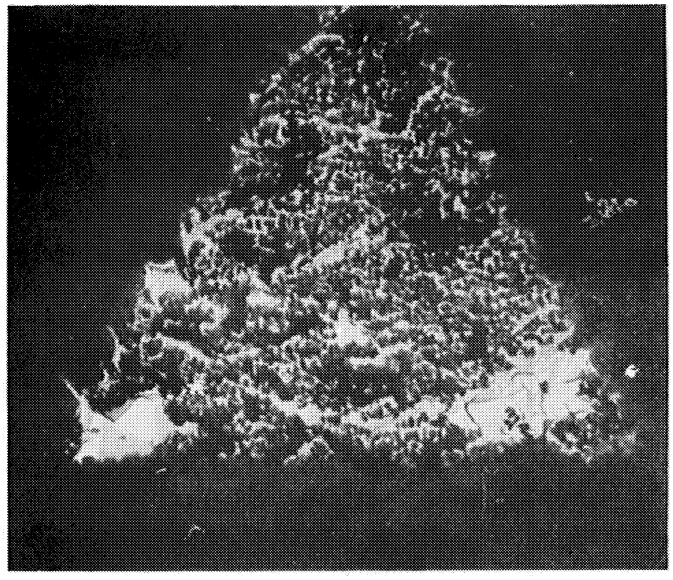
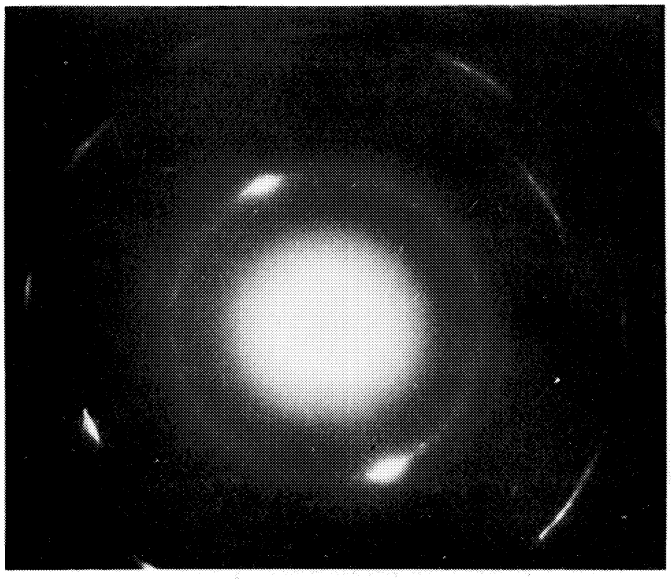


Figure 16. Microphotometer Traces of X-ray Diffractions Films Obtained from Residue of Hydrochloric Acid Extraction.



Extraction replica of γ' from intergranular fracture of Heat 2.



Selected area electron diffraction pattern from area shown above.

Figure 17. - Micrograph and diffraction pattern of γ' phase extracted from experimental heat 2. Extracted particles appear black.

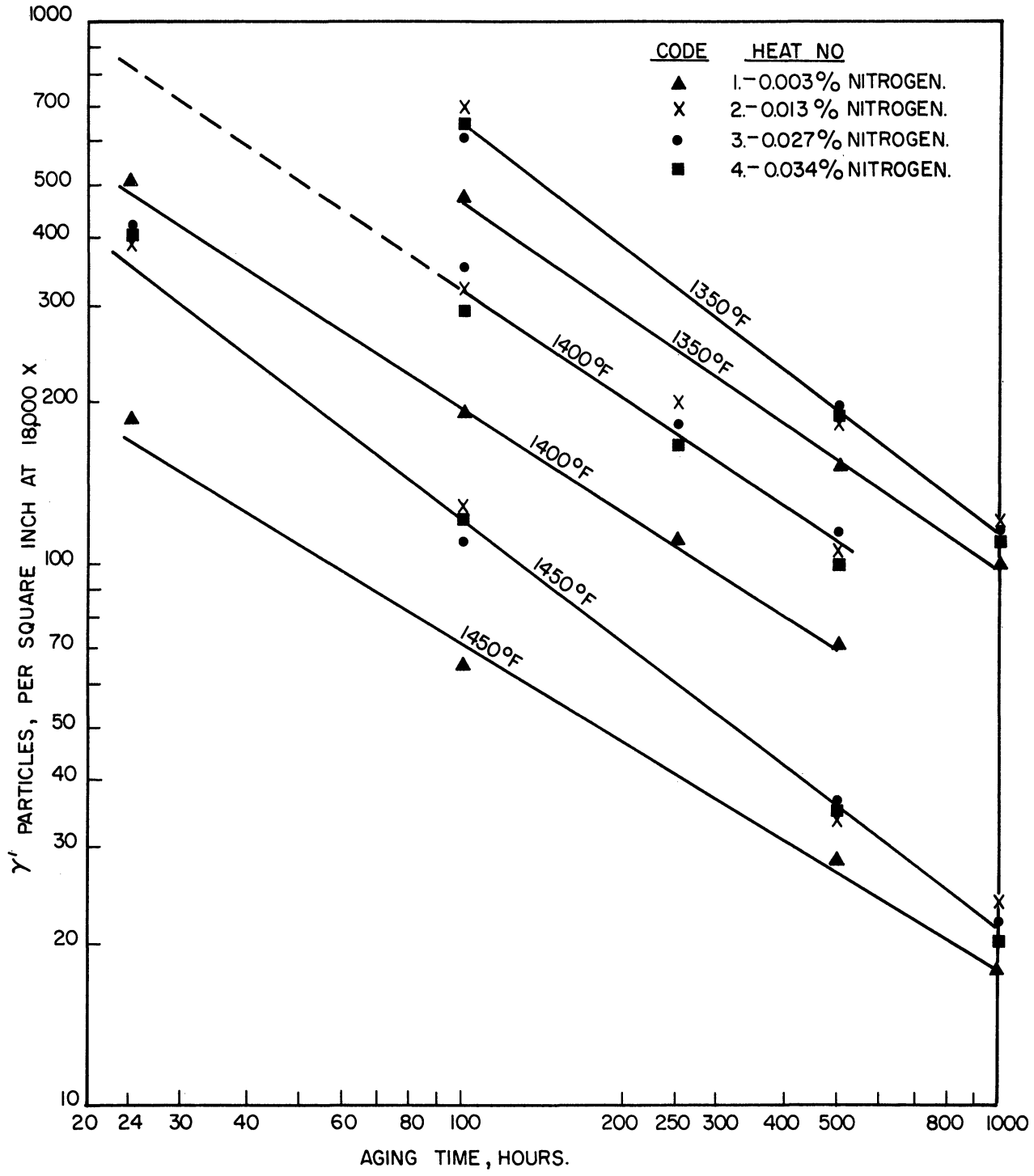
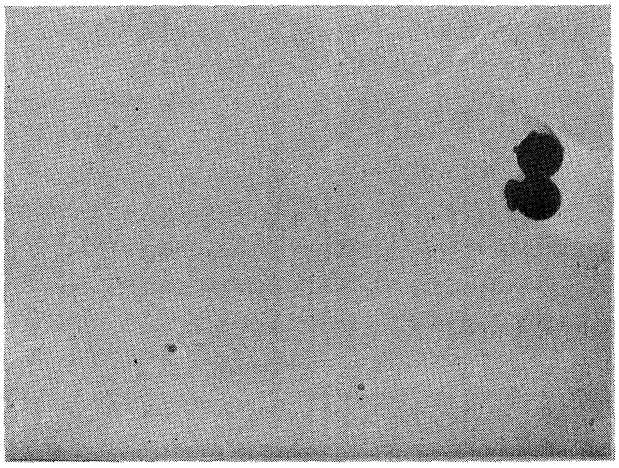
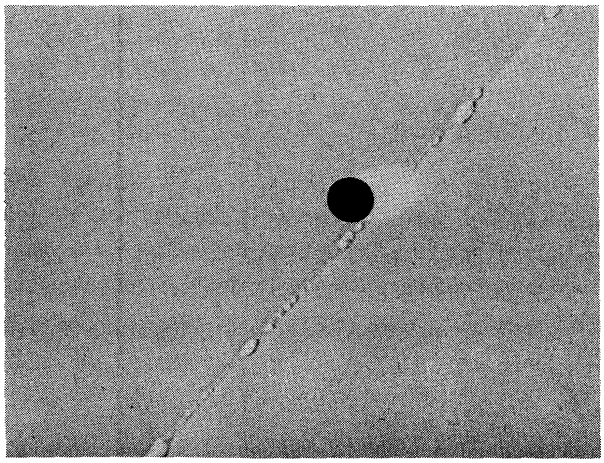


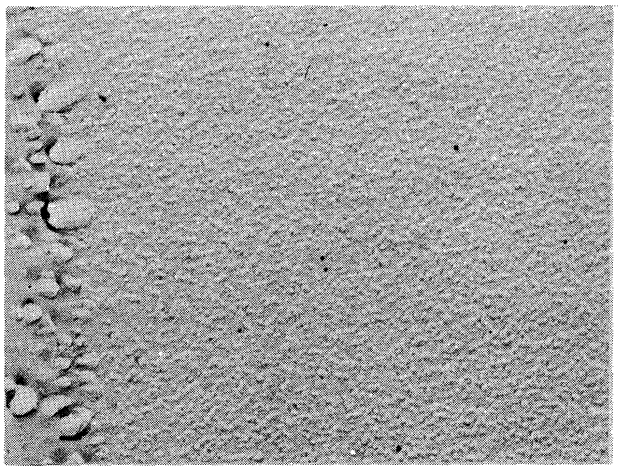
Figure 18. Effect of aging at 1350°, 1400° and 1450°F on γ' particle density for varying nitrogen heats. Heated 4 hours at 2000°F, W. Q. prior to aging.



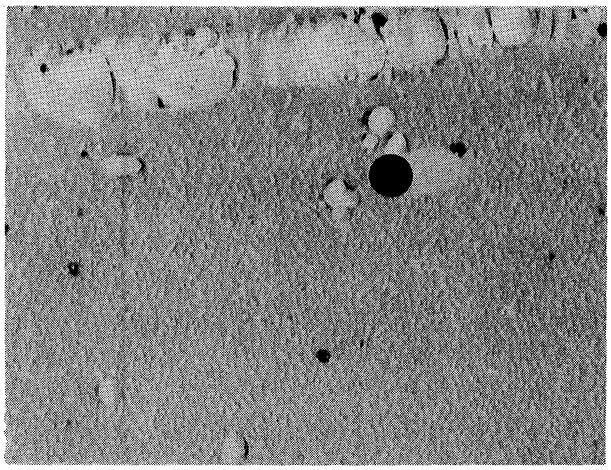
Aged 15 minutes



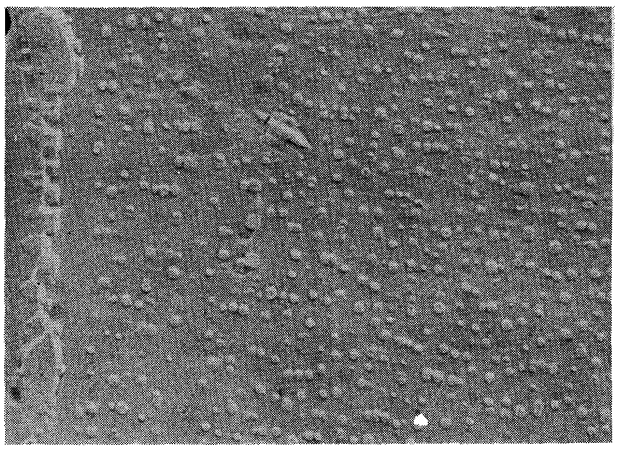
Aged 15 minutes



Aged 100 hours

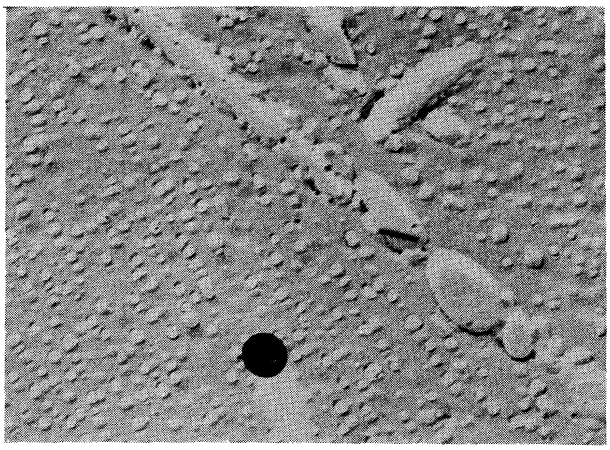


Aged 100 hours



Aged 1000 hours

Heat 1 - 0.003-percent nitrogen



Aged 1000 hours

Heat 2 - 0.013-percent nitrogen

Figure 19. - Effect of aging time on microstructure of experimental heats at 1350°F. Specimens heated 4 hours at 2000°F, W. Q. prior to aging. X18,000.

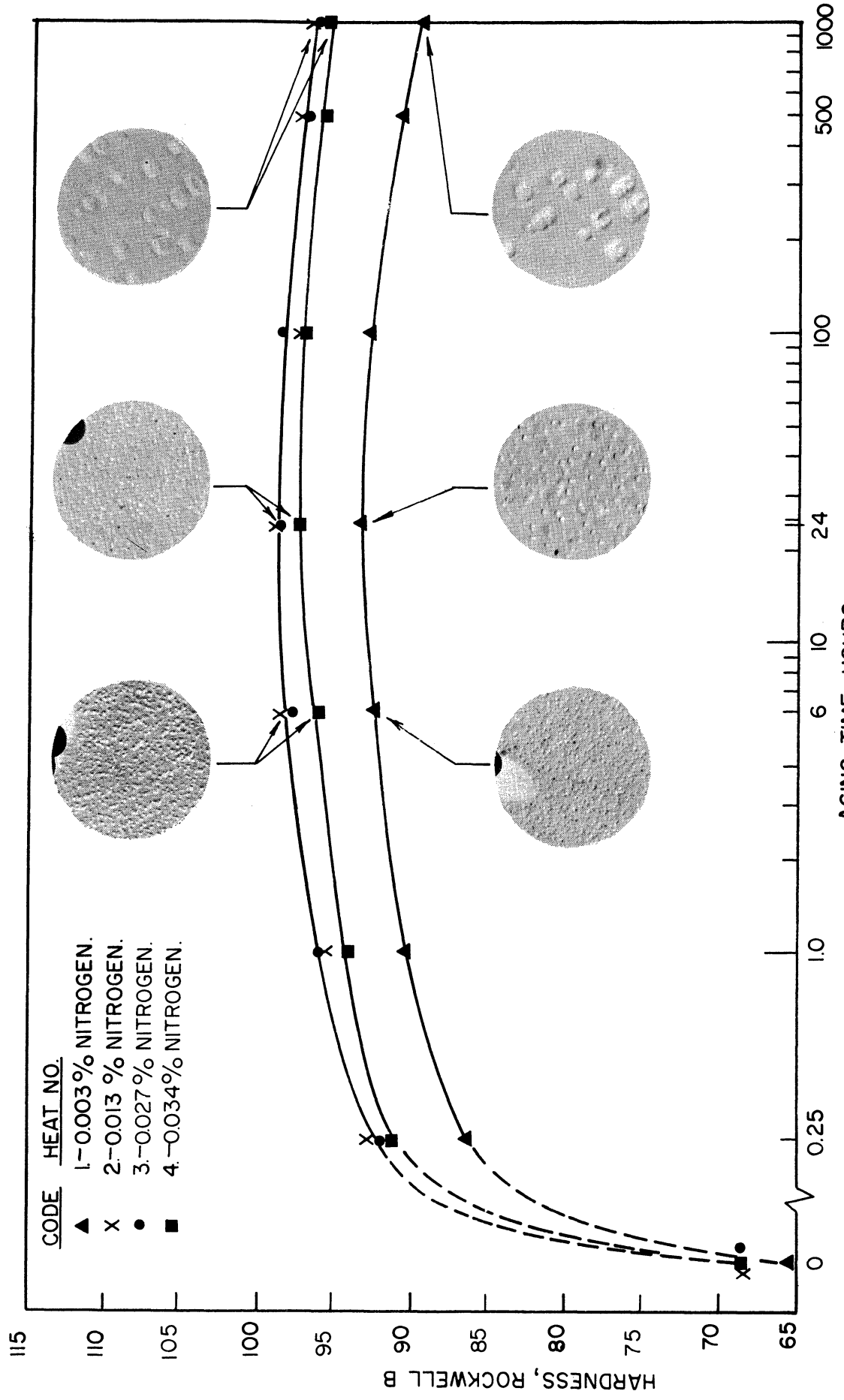
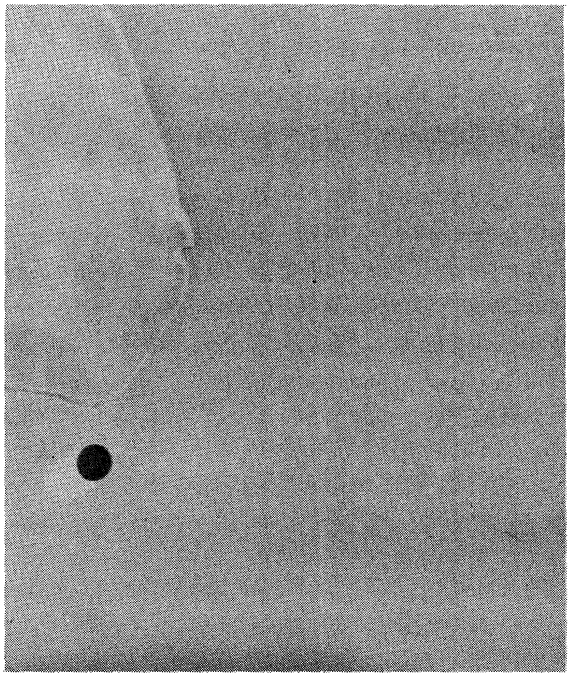
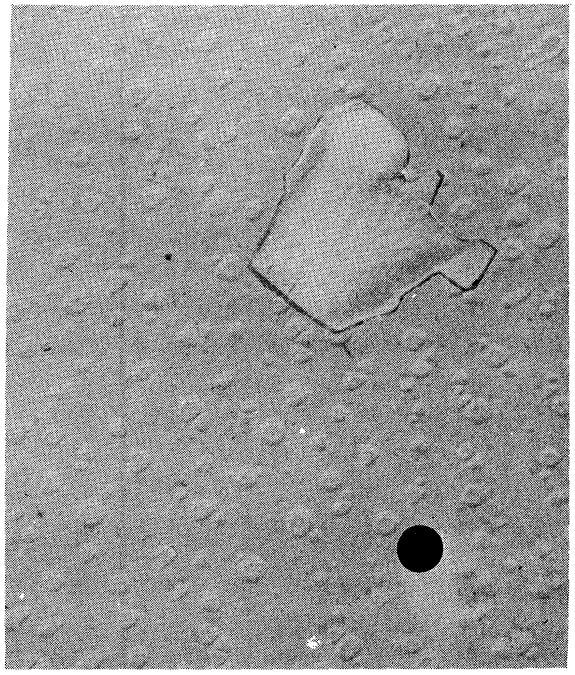


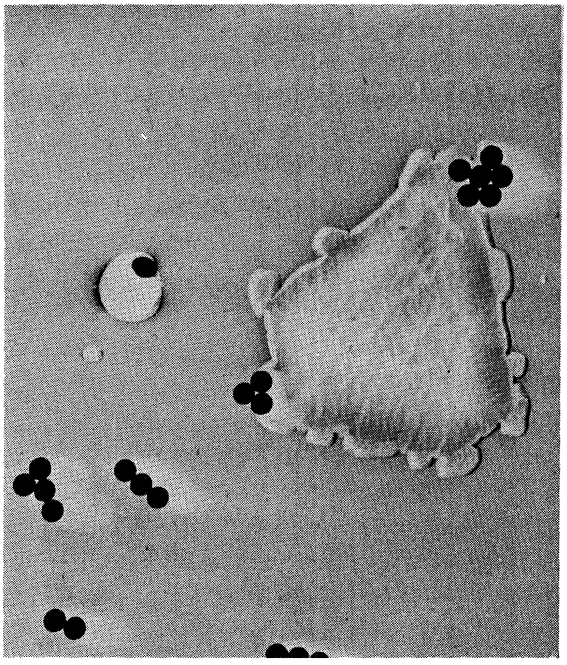
Figure 20. Effect of aging at 1450°F on hardness of the varying nitrogen heats. Heated 4 hours at 2000°F, W. Q. prior to aging. Typical electron micrographs at 18,000X are shown.



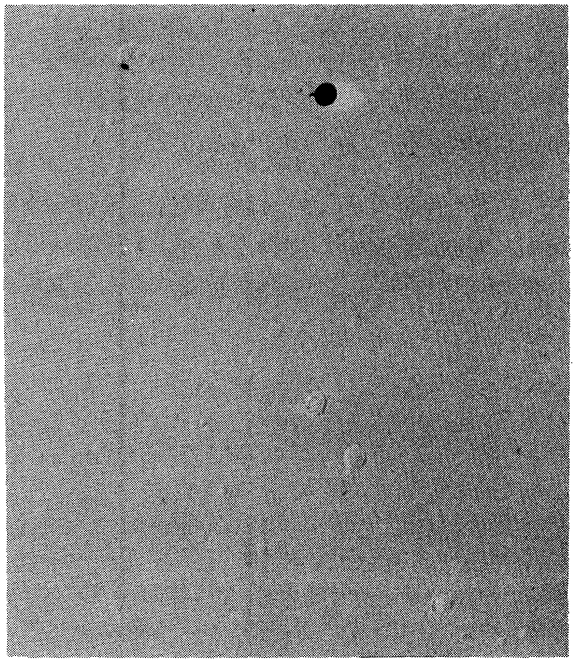
Heated 4 hours at 2000°F, W. Q.
X18,000



Heated 4 hours at 2000°F, W. Q., plus 1000 hours at 1450°F.
X18,000



Heated 4 hours at 2000°F, W. Q., plus 1000 hours at 1450°F, plus 4 hours at 1700°F, W. Q. X12,000



Heated 4 hours at 2000°F, W. Q., plus 1000 hours at 1450°F, plus 4 hours at 2000°F, W. Q. X12,000

Figure 21. - Electron micrographs showing the effect of time and temperature on the occurrence and stability of the phase that precipitated in experimental heats 2, 3, and 4 with long aging exposures.

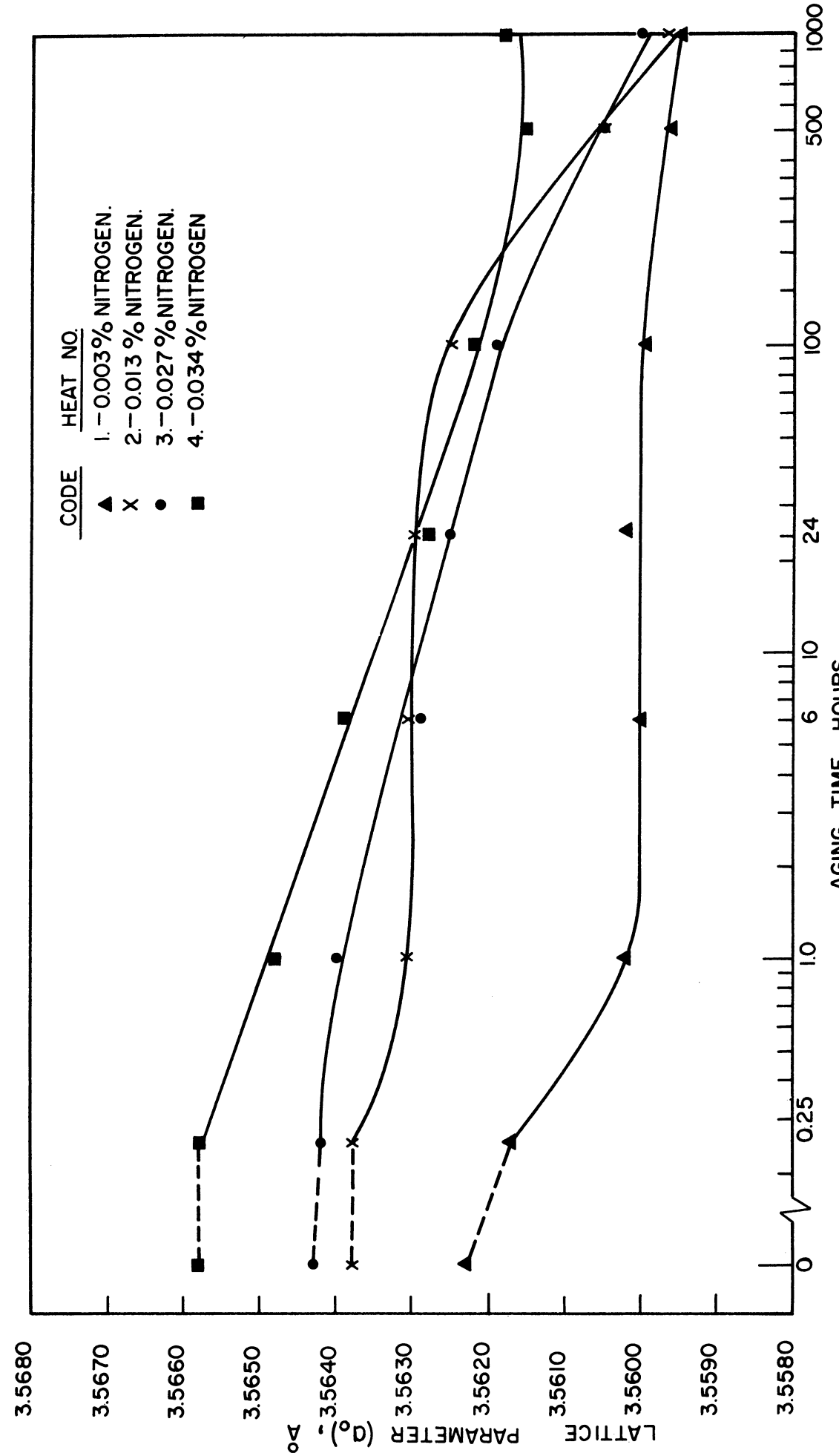
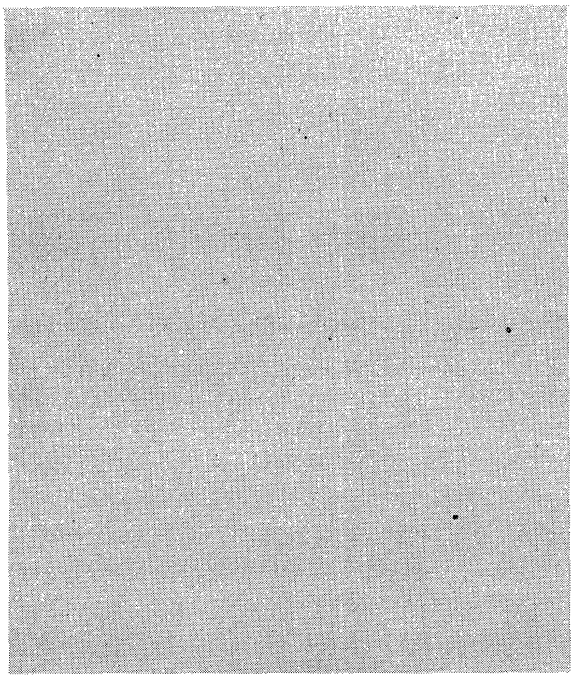


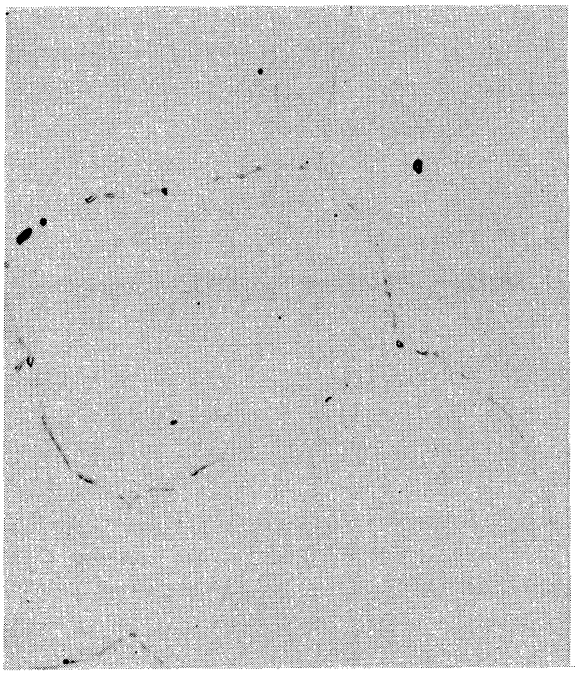
Figure 22. Effect of aging at 1450°F on lattice parameter of the matrix of the varying nitrogen heats. Heated 4 hours at 2000°F, W. Q. prior to aging.



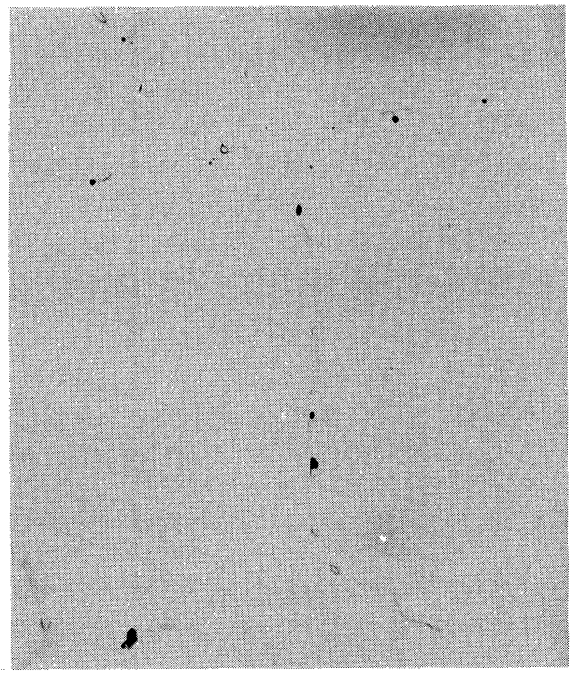
Heat 1 - 0.003-percent nitrogen



Heat 2 - 0.013-percent nitrogen



Heat 3 - 0.027-percent nitrogen



Heat 4 - 0.034-percent nitrogen

Figure 23. - Intergranular precipitation of Cr_7C_3-type carbides in experimental heats. Specimens heated 4 hours at 2000°F, transferred to furnace at 1700°F, held 24 hours, W. Q. X500.

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