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CONTROL OF CREEP-RUPTURE PROPERTIES

OF TYPE 304 (18 Cr - 10 Ni) AUSTENITIC STEELS

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ABSTRACT

A study has been made of the variables influencing the creep-rupture properties of Type 304 austenitic steel as produced for seamless super-heater tube applications. These variables included compositional variations as well as the conditions of heat treatment. This investigation was undertaken to determine the reasons for the higher rupture strength at 1200°F of present day Type 304 steel as compared with material produced in the early 1950's and to provide information which could be used to insure high levels of strength in Type 304 austenitic steel.

The results showed that the creep-rupture strength of Type 304 steel at 1200°F is primarily controlled by the levels of carbon and nitrogen in solid solution. Nitrogen was found to be about 25 percent more potent than carbon as a strengthener.

The difference in the levels of strength of older material and currently produced material is primarily attributed to an increase in nitrogen content from about 0.03 percent to about 0.07 or 0.08 percent. While the exact cause of this difference in nitrogen contents is uncertain, it is likely that small changes in the levels of manganese and nickel resulted in the increased nitrogen contents in the steel.

In low carbon alloys containing up to about 0.14 percent nitrogen there was little effect on the creep-rupture properties at 1200°F due to varying the temperature of heat treatment between 1750°F to 2050°F. The creep-rupture strength of material containing carbon in excess of about 0.05 percent was considerably greater when heat treated at 1950° or 2050°F than when heat treated at 1750°F.

The influence of small amounts of the various residual elements appeared to depend on their "reactivity" with the carbon and nitrogen in solution in the alloy. Titanium (0.03%) reduced the strength of nitrogen bearing heats but increased slightly the strength of low nitrogen, carbon bearing heats Aluminum (0.03%) slightly reduced the strength of nitrogen bearing heats. Molybdenum (0.20%) and copper (0.20%) had almost no effect on the rupture properties at 1200°F.

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INTRODUCTION

Austenitic steels have developed a questionable reputation as a result of a few cases of non-reliability in service. The public utilities, however, use austenitic steels in their steam generators for flexibility of design and for economic service at temperatures and pressures which require materials more heat resistant than the low alloy ferritic steels. Particular interest in Type 304 steel has increased in the last few years because of the high strength exhibited by most of the currently produced material which makes it economically attractive for steam power applications.

Many materials, however, produced prior to about 1955 show considerably lower creep-rupture strengths than are characteristic of more recently produced tube material. The specification for the tubing has not been changed in a way which would account for the increase in strength. Furthermore, it has been known that laboratory heats of Type 304 steel generally have the same low strengths which were characteristic of the older commercially produced material. These factors raise the question of whether or not unrecognized production conditions could occur which would lead to low strength in the alloy. Accordingly, this investigation has been conducted with the intent of obtaining information and developing general principles relating to the high temperature properties of Type 304 austenitic steel as produced for superheater tubing applications. The results should provide the knowledge necessary to insure high levels of strength in the alloy.

The initial direction of the research was centered on the possibility that unknown residual elements might have been present in Type 304 steel which gave rise to the increased strength by a mechanism similar to that found active in Type 321 steel by the SP-6 program.[1, 2]* Preliminary emphasis was placed on the effects of small amounts of nitrogen, titanium and boron on the high temperature properties of the Type 304 alloy.

The influence of other elements was to be evaluated as developing

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* Figures appearing in parentheses pertain to the references at the end of the text.

trends dictated their possible bearing on the problem. The initial results showed nitrogen to have a very marked influence on the creep-rupture properties of this alloy. They showed that nitrogen alone could account for the differences in the level of properties between the alloy produced in the early 1950's and the present day commercially produced material. Consequently, a concentrated effort was initiated on the influence of this element. This study, however, was complicated by the fact that reliable analyses for nitrogen were not available until late in the program.

As a result of the magnitude of the effort directed toward nitrogen, fewer elements were studied than were originally anticipated. Some work was done on the effects of small amounts of aluminum, molybdenum and copper. Using the high temperature data developed, along with thermo-dynamic considerations, it was possible to speculate as to the types of effects that may result from small amounts of other elements.

The 1000-hour rupture strength at 1200°F has been the primary basis for the evaluation of the influence of the experimental variables. Where necessary or desirable, these data have been supplemented with rupture data at 1350°F and with other experiments.

This investigation was carried out in the Department of Chemical and Metallurgical Engineering of the University of Michigan College of Engineering under the sponsorship and with the financial assistance of the Edison Electric Institute.

EXPERIMENTAL PROCEDURES

Materials

Vacuum induction-melted laboratory heats were primarily used to attain the objectives of this investigation. In addition, tubing from commercial heats was utilized for purposes of comparing the responses of laboratory and commercially produced alloys to specific test conditions.

Commercial Material. The commercial materials were in the form of ½-inch wall seamless tubing and were carried over from the SP-6 investigation. [1] Detailed chemical analyses of these materials appear in Table I. The tube coded PT-9 was chosen as being representative of the current high strength commercial material and received primary attention in this study.

A typical fabrication procedure for this material would be as follows:

1. The billet was hot pierced at 2100°F to a tube blank approximately 4 inches outside diameter by 3/4-inch wall thickness.

2. The tube blank was then annealed for about 15 minutes at 1900-2000°F, followed by a water quench.

3. The blank was pickled, straightened and "conditioned".

4. The tube blank was finally "tube reduced" or "roto-rocked" to a seamless tube 3.0 inches in outside diameter by 0.50-inch wall thickness.

Laboratory Heats - Preparation. The laboratory heats were vacuum induction-melted in fused magnesia crucibles using a charge consisting of 5000 grams (approximately 10 pounds) of virgin melting stock. The initial melting took place under a pressure of less than 10 microns of mercury. The heats were deoxidized with spectrographic grade carbon which was added to the initial charge in the form of powdered graphite.

In order to avoid excessive losses of manganese through vaporization, this element was added to the charge after the initial meltdown had been completed. For the purpose of making this addition an atmosphere was introduced into the vacuum chamber to a pressure of 200-500 microns.

In those heats to which nitrogen was added, the atmosphere used for the manganese addition was dried nitrogen gas. After the manganese addition was completed the pressure of nitrogen over the melt was raised to ½ atmosphere and an addition of CrN was made. The presence of the nitrogen atmosphere over the melt helped insure a predictable nitrogen recovery.

A short time was allowed after the additions were made for homogenization of the molten metal. Half of the molten metal was then poured into

a 2-inch diameter ingot mold. A further alloy addition was then made to the molten metal remaining in the crucible and the second ingot poured. The resultant cropped ingots were approximately four inches in length and weighed about three and one-half pounds.

These ingots were rolled into $\frac{1}{2}$-inch square barstock. This processing was designed to roughly simulate the production of seamless tubing by the "tube reducing" process. The following procedure was used:

1. The ingots were heated for $1\frac{1}{2}$ hours at the rolling temperature of 2150°F.

2. The ingots were hot reduced approximately 70 percent to 1-inch square bars using 10 to 13 passes with 3 or 4 reheats.

3. The hot rolled bars were then cold reduced 50 percent in cross-sectional area to about 0.7-inch square bars.

4. The cold-rolled bars were heat treated for $\frac{1}{2}$-hour and water quenched.

5. The bars were then given a final cold reduction of 50 percent in cross-sectional area to $\frac{1}{2}$-inch square barstock.

Samples for chemical analyses were taken from the center portion of the hot-rolled barstock.

Laboratory Heats - Description. Chemical compositions of the laboratory heats are given in Table II. Complete chemical analyses of all the laboratory heats were not made due to the high cost. Certain key heats were analyzed completely and spot checks were made for various elements in other heats. All analyses were made by commercial analytical laboratories. At least one of the two ingots from each heat was analyzed for carbon. The remainder of the composition data was inferred from the reported analyses, the aim composition and knowledge of recovery efficiencies. These data are tabulated in Table II. For the most part, this procedure appears to be quite adequate since the losses of elements such as nickel, chromium, silicon and manganese are very small (usually less than 3 percent of the aim concentration).

Nitrogen analyses were accomplished by wet chemical techniques and measured total nitrogen content. In the presence of strong nitride formers

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such as titanium, this technique apparently requires considerable care and skill, however, consistent and reasonable results were obtained. These results, however, indicated that nitrogen had been picked up from the nitrogen atmosphere in the furnace. Rapid nitrogen pick-up under atmospheric pressures was later found to have been noted by several authors,[3, 4] for chromium bearing alloys in general and for Type 304 steel in particular. Using the data reported for several heats, the nitrogen contents for the remainder of the heats were estimated. This involves greater error than the estimates of chromium, nickel, etc. The error in the estimated nitrogen contents of Table II is believed to be not more than $\pm$ 0.02 percent nitrogen.

Creep-Rupture Tests

The creep-rupture tests were conducted in simple beam or in direct loaded individual creep-rupture units using test specimens with a 0.250-inch diameter and a 1-inch long reduced section. Three chromel-alumel thermocouples were wired to the 1-inch reduced section of the specimens with chromel wire. Type 304 steel foil 0.005-inches thick was placed between the thermocouple and the specimen body to help reduce the harmful effects occasionally associated with the contact of alumel wire with the specimens.[5] The thermocouples were wrapped tightly with asbestos cord. The temperature variation along the reduced section was held to less than 3°F while the indicated test temperature was controlled to within $\pm$ 3°F. Test specimens were placed in a hot furnace, brought to temperature and loaded within a period of about 1 hour. This procedure requires close attention during the first hour of the test but minimizes any possible effects of microstructural instability.

Creep strain measurements were taken during the tests using a modified Martens-type mirror extensometer having a sensitivity of 0.00001 inch.

The percent elongation of the rupture specimens was based on the change in thread-to-thread measurements. The reduction of area measurements were based on the change in cross-sectional area of the specimens.

The techniques used in this investigation for structural examination included optical and electron microscopy as well as X-ray and electron diffraction analyses of extracted residues.

Specimen Preparation. Specimens for microscopic examination were sectioned longitudinally along the center line of the barstock or the creep-rupture specimens using a water-cooled cut-off wheel. The specimen was then mounted in Bakelite and mechanically polished on wet silicon carbide paper wheels. Final polishing was accomplished using a 6 and 0.5 micron diamond pastes, in turn, on cloth-covered rotating wheels, followed by Linde "B" alumina powder in aqueous suspension on a vibratory polisher.

Etchants. The following etchants were used for various purposes throughout the investigation:

1. 60-percent HNO_3, electrolytic. This etch satisfactorily revealed carbides, sigma phase, grain and twin boundaries and concentration variations in 18Cr-10Ni alloys.

2. 10-percent chromic acid, electrolytic. This etch was useful for revealing carbide phases.

3. 60-percent phosphoric acid, electrolytic. This etch was particularly suited for high resolution of fine carbide precipitates.

4. 10N-KOH, electrolytic. This etch was primarily used to identify sigma phase.[11]

5. Vilella's reagent (HCl and picric acid in alcohol), immersion etch. This etch was used to reveal sigma phase and carbides.

Electrolytic etching was accomplished using a platinum electrode with an applied potential 1 to 3 volts and a current density of about 0.5 amperes per square inch for between 5 and 30 seconds.

Microscopy. Conventional methods were employed for optical examination. Electron microscopy was carried out using collodion replicas

of the etched metal surface. The replicas, supported by fine nickel screens, were shadow cast with paladium to increase contrast. A JEM-6A electron microscope was used in this investigation for examination of the replicas.

Diffraction. Extractions of minor phases from the specimens were made using a mixture of HCl and picric acid as the extracting medium. Portions of residues from the extraction were used for selected area electron diffraction studies. Some of the residues were "rolled" into filaments using a Duco cement binder and used to make X-ray power patterns for the identification of the extracted phases.

RESULTS

Creep-Rupture Properties

The creep and rupture data accumulated during this program are tabulated in Table III. From these data the 1000-hour rupture strength, the slope of the stress-rupture time curve and the estimated elongation and reduction in area at rupture in 1000 hours have been determined for all the materials and are presented in Table IV. The results, as a function of compositional variables, can be summarized as follows:

Influence of Carbon. Laboratory heats available from other sources[1, 6] supplemented by heats made in the present investigation provided a series of heats with variations in carbon content from 0.009 to 0.14 percent in the base alloy (18.5%Cr - 10.5%Ni - 1.5%Mn - 0.5%Si). No addition of nitrogen was made to any of these heats. The 1000-hour rupture strengths and the estimated ductilities (elongation will be used as the measure of ductility unless otherwise stated) at rupture in 1000-hours of these heats are shown in Figure 1. The following points concerning the role of carbon are considered to be significant:

(a) There was a general increase in the level of strength with increasing carbon content up to about 0.10 percent carbon for heat treatments at 1950° and 2050°F. The data indicated no significant increase in strength of the alloy when the carbon content exceeded this level.

(b) There was no appreciable difference in rupture strength or ductility of the alloys with variable carbon contents when heat treated at 1950° or 2050°F.

(c) At carbon contents less than about 0.05 percent, the 1000-hour rupture strengths were slightly lower when heat treated at 1750°F than when heat treated at 1950°F. Material heat treated at 1750°F tended to increase in strength with increasing carbon content, but only up to about 0.05 percent carbon.

(d) The rupture strength of the alloys heat treated at 1750°F tended to decrease slightly with increasing carbon content above 0.05 percent.

(e) The estimated rupture ductility at 1000 hours decreased with increasing carbon content for heat treatments of 1950°F and 2050°F. The decrease was most rapid for the first few hundredths percent carbon. At higher carbon levels there was little change in ductility.

(f) The ductility of the materials heat treated at 1750°F was greater than that of the materials treated at 1950° or 2050°F. The rupture ductility, however, followed the same decreasing trend for the first few hundredths percent carbon, as was noted for the solution treatments at 1950° and 2050°F. Above 0.05 percent carbon the rupture ductility increased with increasing carbon content.

Influence of Nitrogen. The 1000-hour rupture strengths of laboratory heats with varying nitrogen contents heat treated at 2050°F are shown in Figure 2. The data of Nakagawa and Otoguro[7] are also shown for comparison. Figure 3 shows the influence of various heat treatments on the stress-rupture time curves of heats containing high nitrogen with low and normal carbon (Heats 1343A with 0.145%N, 0.02%C and 1341A with 0.08%N and 0.06%C). Data from Heat 1310A (with 0.01%N and 0.009%C) have also

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been included and serve as a base for comparison with data from other materials. The minimum creep rates of several of these alloys are plotted versus stress in Figure 4 and versus rupture time in Figure 5. These data indicate the following:

(a) Increasing the nitrogen content of the laboratory heats greatly increased the 1000-hour rupture strength. This was true for all carbon levels studied, i.e. between 0.01 and 0.14 percent carbon.

(b) The increase in strength arising from a given nitrogen addition was greater than that due to the same amount of carbon.

(c) Nitrogen, up to at least 0.14 percent, appears to be beneficial as a strengthener. No well-defined limit to the increase in rupture strength due to increasing nitrogen content has been established, however.

(d) The ductility of alloys decreased with increasing nitrogen content. The magnitude of this decrease appeared to be only slightly greater than that resulting from similar increases in carbon content. The combined effects of nitrogen and carbon in decreasing the ductility of the laboratory heats were somewhat greater than that which would be accounted for by the independent effects of these elements.

(e) Heat treatment at 1750°F was less detrimental to the creep-rupture strength of an alloy containing nitrogen and low carbon (Heat 1343A) than to heats with higher levels of carbon. This is reflected both in the stress-rupture time curves (Figure 3) and in the stress-creep rate curves (Figures 4 and 5).

(f) The slopes of the log stress-log rupture time curves of heats containing nitrogen and carbon did not vary significantly among different heat treatments and testing temperatures.

Influence of Boron and Titanium. The 1000-hour rupture strengths and the estimated rupture ductilities at 1000 hours are tabulated in Table V for the laboratory heats containing small amounts of titanium (0.02 - 0.05%) and/or boron (15 ppm) in addition to carbon and/or nitrogen. The properties of these heats are compared in this table with the properties of similar heats

with no boron or titanium additions. The data shown in Table V are for materials tested at 1200°F after heat treatment for ½-hour at 2050°F, W. Q. The influence of varying heat treatments on the stress-rupture time curves of alloys with boron and titanium additions is shown in Figure 6. The response to heat treatment of the alloys containing nitrogen plus low carbon, nitrogen plus normal carbon, nitrogen plus boron plus titanium and nitrogen plus normal carbon plus boron plus titanium are compared in Figure 7. The creep rate data for several alloys containing additions of only carbon and nitrogen, heat treated at 2050° and 1750°F, are presented as a function of stress in Figure 4; these data can be compared with data obtained from other alloys containing carbon, nitrogen, boron and titanium which are also shown in Figure 4. The following observations can be made regarding the influence of boron and titanium:

(a) The alloys with boron (but not titanium) showed little or no change in the 1000-hour rupture strength as compared with similar heats without boron when tested at 1200°F after heat treatment for ½-hour at 2050°F. In general, the ductility of these alloys was somewhat improved as the result of the boron addition.

(b) The 1000-hour rupture strength was altered in the alloys to which titanium was added (no boron). The strength alteration is apparently related to the presence of carbon and/or nitrogen:

(1) For the heat with very low carbon and nitrogen contents (Heat 1364A) 0.03 percent titanium increased the rupture strength by a small amount. With a higher carbon content (Heat 1344A) the degree of increase in strength was greater.

(2) The addition of 0.03 percent titanium to the heat containing about 0.12 percent nitrogen (Heat 1344B) decreased the 1000-hour rupture strength.

(3) The estimated ductility at rupture in 1000 hours of heats with the titanium additions was generally greater than in similar heats without titanium.

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(c) For the heats with low carbon and nitrogen contents (<0.02%), there was little or no difference in strength as the result of additions of 0.03 percent titanium plus 15 ppm boron or additions of the titanium alone.

(d) In the heats containing carbon and/or nitrogen (>0.05 percent), there was a significant improvement in the 1000-hour rupture strength resulting from the combined addition of 0.03 percent titanium and 15 ppm boron. The strength of a heat to which 30 ppm of boron was added (Heat 1339B), however, was not as great as the similar heat with only 15 ppm boron added (Heat 1339A). The ductilities of these alloys were lower than those alloys with separate additions of titanium and boron, however, the ductilities of all the alloys were in excess of 10 percent.

(e) From Figure 6 it can be seen that the higher 1000-hour strengths at 1200°F of the heats with both boron and titanium additions may not be retained at times beyond 1000 hours. The stress-rupture time curve for the heat with boron, titanium, nitrogen and carbon (Heat 1339A) underwent a change in slope just beyond 1000 hours. The slopes at longer times have been constructed to be parallel to the slope of the material tested at 1350°F, which is significantly steeper than the shorter time slope noted at 1200°F. This slope is noticeably steeper than the slope of other alloys tested at 1200° or 1350°F. The rupture tests at 1200°F indicate that the heat with boron, titanium and nitrogen (Heat 1338B) also underwent a change in slope; the heat with boron, titanium and carbon (Heat 1337A) apparently did not.

(f) The stress dependence of the minimum creep rate for the heats containing boron and titanium appears to be different from that of the heats without either of these additions. This is seen in Figure 4. The reciprocal slope, $\underline{n}$, of the log stress versus the 1200° or 1350°F minimum creep rate curve (i.e. the change in creep rate with change in stress) was between 6 and 7 for the heats without titanium and boron when heat treated either at 2050° or 1750°F. For the heat with titanium and

boron (Heat 1339A) the value of $\underline{n}$ was also between 6 and 7 except when the alloy was heat treated at 2050°F and tested at 1200°F under high stress where $\underline{n}$ was approximately 13.

Influence of Manganese. The manganese level of the laboratory heats was intended to be about 1.50 percent, approximately the level of present-day production heats for seamless tube and pipe. One of the heats analyzed contained only 0.81 percent manganese (Heat 1366). There was no difference in the properties of this heat which could be attributed to the lower manganese level, although this conclusion is clouded by the addition of 15 ppm of boron. Heats 1281 and 1282[1, 6] with no nitrogen added had 0.44 and 1.48 percent manganese respectively with no significant difference in their 1000-hour rupture strength (see Table IV).

Two alloys (Heats 1340A and 1340B) were made to which no manganese was added. The properties were significantly different from similar heats which contained manganese. The nickel contents of the very low manganese heats were increased in order to maintain a wholly austenitic structure. One ingot had a low carbon content (0.01 percent) while the other had a slightly higher carbon level (0.04 percent). Both ingots had nitrogen additions. The 1000-hour rupture strengths of Heats 1340A and 1340B were 17 and 18 ksi respectively. This compares with values of 23 to 24 ksi for similar heats with 1.50 percent manganese. These heats had relatively low ductility at rupture (see Table II or III). In addition the stress dependence of the minimum creep rate was considerably difference from the other heats, $\underline{n}$ being about 14 in contrast with values of about 6 to 7 for similar heats with approximately 1.50 percent manganese (see Figure 4).

Influence of Aluminum. The data from the four heats to which 0.02 to 0.03 percent aluminum was added indicate that under certain conditions aluminum can have a significant effect on the properties of 18Cr-10Ni material. The data, however, were not extensive enough to clearly define the level of the effect. The rupture data for material heat treated at 2050°F and tested at 1200°F are shown in Figure 8. Two of the heats containing small additions of titanium are also shown for comparison. Based on these

(a) For the heat with the normal carbon and no nitrogen (Heat 1360A) there was no influence of the aluminum addition on the properties of the material.

(b) The addition of aluminum to a heat containing normal carbon (0.06 percent) and about 0.13 percent nitrogen (Heat 1358B) resulted in a decrease of the 1000-hour rupture strength from 25 ksi to 20.3 ksi. The slope of the stress-rupture time curve of this heat was slightly steeper than exhibited by the similar heat (Heat 1342B) without aluminum.

(c) The addition of aluminum to a heat containing low carbon (<0.02 percent) and 0.12 percent nitrogen (Heat 1358A) resulted in lower 1000-hour rupture strength than for a similar heat without aluminum (Heat 1343A).

(d) The addition of aluminum to a heat with 0.08 percent carbon and 0.12 percent nitrogen and 15 ppm boron (Heat 1360B) did not significantly alter the short time strength. The slope of the stress-rupture time curve, however, was lower (it is comparable to that of heats with boron titanium and nitrogen, Heats 1338B and 1339A) with the result that the 1000-hour rupture strength of this alloy was higher than that of a similar aluminum-bearing alloy without the boron addition.

Influence of Copper and Molybdenum. One heat was prepared containing 0.20 percent copper (Heat 1365A), approximately the amount found in many commercial materials. Rupture tests at 1200°F showed an insignificant decrease in strength compared with heats without copper; compare, for instance, Heat 1365A with Heat 1342B in Table IV. Nowak[8] has also reported that copper has no effect at levels below 0.30 percent.

A heat similar to the above was prepared but with the further addition of 0.20 percent molybdenum (Heat 1365B). This is about the level of residual molybdenum found in many commercially produced Type 304 heats. Rupture tests of this heat at 1200°F indicated no significant improvement in strength attributable to the molybdenum present.

A higher molybdenum level (2.0 percent) was shown[1] to increase

the 1000-hour rupture strength at 1200°F of a low carbon - low nitrogen heat (Heat 1310B) to about 18,000 psi from a value of 12,500 psi for a similar heat without molybdenum (Heat 1310A). Nakagawa and Otoguro[9] have recently reported on the influence of molybdenum in an 18 Cr-12 Ni alloy. They indicated an increase in the creep and rupture strengths of the material as the result of additions of molybdenum in the range from 0.85 to 3.70 percent.

Microstructural Examination

Samples of the materials were taken for optical and electron microscopic examination. The microstructural characteristics of the grains and of the grain boundaries are controlled by somewhat different processes. These characteristics will be discussed in separate sections.

Grain Structure. The salient features of the grains of materials heat treated above 1800°F and tested at 1200°F appear to be primarily dependent on the carbon and nitrogen content. The points to be emphasized are as follows:

(a) With very low carbon or nitrogen contents, there was little evidence of precipitation within grains. The grains were inherently soft and deformed readily. This resulted in high rupture ductilities. Typical of this behavior were Heats 1310A, 1338A, 1363A and 1364A. Photomicrographs of rupture specimens of Heats 1310A and 1338A are shown in Figure 9.

(b) With carbon present the structure showed carbide precipitates within the grains often along slipped planes. This precipitation was generally not optically visible until the testing time exceeded about 100 hours. The extent of this precipitation depended on the carbon level and upon the place within the specimen where the precipitation occurred. The precipitation was most intensive near the fracture and decreased toward the shoulder of the specimen. This is illustrated in Figures 10a and

10b for Heat 1309B. In these figures the specimens were etched with chromic acid which revealed carbides and sigma phase. This structure was typical of heats containing 0.04 percent or more carbon. The fine carbide precipitates appeared to form on dislocations. This can be seen by the 'pile-ups' on slipped planes near the boundaries in Figure 10b. The variation in precipitate density from the fracture to the threaded section of the specimen (i.e., from a high stress to a low stress region) was also indicative of precipitation on dislocations. Finally, and in contrast to the heats with low carbon or nitrogen, the grains of the heats containing carbon in solution before testing were not markedly deformed.

(c) For heats containing high nitrogen and low carbon, the various etchants did not reveal discrete precipitation on slipped planes as was visible when carbon was present. However, slip and multiple slip were occasionally visible within the grains. These features are seen in the photomicrographs of ruptured specimens of Heats 1361A, 1343A and 1343B which are shown in Figure 11. It was further observed that the grains of specimens from these heats were not markedly deformed, indicating that the grains had been strengthened even though no precipitation was visible.

(d) Other compositional variations did not appreciably alter the features described above, although other microconstituents also may have been present. In alloys to which titanium was added (0.03-0.05%), titanium carbonitrides or titanium nitrides were usually present in stringers. The titanium carbonitrides were generally fewer in number and more uniformly dispersed in the heats containing boron than in those heats without boron. In the heats with carbon and nitrogen present, there were many more small particles present in the grain boundaries after testing when titanium was also present than when titanium was absent. These particles may have been titanium compounds or possibly sigma phase.

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In specimens which were heat treated at low temperatures, i.e. 1750°F or lower, the microstructural characteristics were somewhat different from those of specimens heat treated at higher temperatures. In general, alloys containing carbon did not develop extensive precipitation on slipped planes when tested after a low temperature heat treatment. There was precipitation of carbides, but many of these carbides were located on the original cold worked structure and in the grain boundaries. Most of these carbides were formed during the heat treatment, not during testing. These features can be seen in Figure 18d and 18e (also see Figure B-2).

Grain Boundaries. The appearance of the grain boundaries in the alloys heat treated above 1800°F before testing was characterized by an apparent "thickening". The "thickening" was not found to correlate with the creep-rupture properties of the materials tested, however, it is believed to be connected with some of the processes occurring during creep exposures, such as carbide precipitation and sigma phase formation. In various instances it is difficult to distinguish whether the "thickening" is due to a new, continuous phase formed at the boundaries or to concentration gradients present at the boundaries. An example is shown in Figure 10c. The etching reagent used on this specimen was 60 percent HNO_3. Figure 10a shows the same specimens etched with chromic acid and illustrates that the boundary "thickening" phenomenon was not revealed with equal clarity with all etchants. Further observations of the grain boundary characteristics are as follows:

(a) The extent of the "thickening" varied within the specimen. It was most marked near the fracture and decreased toward the shoulders of the specimen. Figures 10c and 10d show a typical example of this. This characteristic implied that the phenomenon producing the "thickening" was stress and/or strain induced.

(b) The extent of "thickening" increased with increasing testing time (at 1200°F). Figure 12 shows the development of the thickened boundaries in Heat 1338B over the time period from 33 to 4300 hours.

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(c) A specimen, 38B-1, which showed the largest amount of the boundary "phase", was cold worked and recrystallized (at 1400°F) in an attempt to move the grain boundaries away from the "phase". This was done primarily to differentiate between two possible cases:

(1) That this new "phase" was recrystallized austenite of about the same composition as the matrix, or

(2) That "thickening" was simply the result of a concentration of one or more elements in the alloy.

The result of this experiment is shown in Figure 13a. This micrograph shows new recrystallized grain boundaries and sharp concentration changes where the old grain boundaries had been.

(d) Efforts to determine the nature of this "phase" by X-ray techniques were unsuccessful. An eletron microprobe examination did not reveal the nature of the "phase" but did imply that the areas around the boundaries were depleted of chromium.

(e) It was also observed (see Figure 13b) that the "thickened" boundaries were continuous with depleted areas at oxidized surfaces of the specimen. The oxides formed at 1200°F on 18Cr - 10Ni type material were primarily chromium or possibly complex, chromium-rich, iron oxides. This implies that the metal areas adjacent to the oxides were depleted of chromium. The continuity between these areas and the boundary areas implies that the thickened boundary area was chromium depleted austenite. The localization of the depletion at the boundaries is probably due to the greater diffusivity of substitutional atoms at boundaries or interfaces than within the matrix.

(f) The possible occurrence of sigma phase in the boundaries was verified using several types of etching reagents.[10, 11] 10N KOH used electrolytically was found to distinctly reveal sigma phase by a staining process. This etch showed particles of sigma phase to be located in the grain boundaries. Figure 14a shows an area of specimen 38B-1 etched with KOH. This is followed by a photomicrograph of the same specimen re-etched using 60 percent HNO$_3$ in Figure 14b. The for-

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mation of sigma phase could account for all or part of the chromium depletion adjacent to the boundaries. It should be noted that carbide precipitation could also account for some chromium depletion.

(g) In specimens tested at 1350°F the boundary thickening was less distinct than in specimens tested at 1200°F. Specimens of Heat 1341A tested at 1200°F and 1350°F are compared in Figure 15. This feature can be accounted for by considering that:

(1) There was less sigma phase formation at 1350°F to cause depletion than occurred at 1200°F. Carbide formation may have caused some chromium depletion, as is evident around the carbides within the grains of various samples.

(2) Diffusion of substitutional atoms (Cr) at 1350°F from within the matrix to the boundaries was sufficiently rapid to compensate for chromium depletion near the boundary.

(h) Figure 16 shows various other heats having wide compositional variations which exhibit boundary "thickening" during testing at 1200°F. These photomicrographs are from rupture specimens which lasted between 500 and 1000 hours. Note that in some of the micrographs there appears to be boundary migration within the nickel-rich area.

(i) Electron micrographs of several samples etched to show the boundary phenomenon are shown in Figure 17. The distinctive feature visible was that the edges of the thickened boundary regions appeared as gradual transitions rather than sharp phase boundaries. The actual grain boundary was often visible within the thickened regions as a sharp line. Occasionally the boundary was coincidental with one edge of the thickened region. In such a case the boundary is assumed to have migrated away from its original position.

In some cases the appearance of the grain boundaries in material given a low temperature heat treatment (i.e. 1750°F or lower) prior to testing at 1200°F was significantly different from that after higher temperature heat treatment. Figure 18 shows a series of photomicrographs from ruptured

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specimens (600 to 800 hours duration) of a commercial tube, PT-9, cold reduced and heat treated at 1800°, 1700° and 1600°F before testing at 1200°F. The specimen heat treated at 1800°F was very similar in its microstructure to a specimen solution treated at 2050°F and tested at 1200°F. The specimen heat treated at 1700°F, however, contained massive particles of sigma phase and exhibited considerably wider boundaries. These regions gave the appearance of being a distinct phase. This was further accentuated in the specimen heat treated at 1600°F. As was noted with the specimens heat treated at 2050°F, the amount of the boundary "phase" progressively decreased as one moved away from the region of the fracture. This can also be seen in Figure 18.

The amount of boundary "phase" in other materials heat treated at 1750°F appears to be less than that found in PT-9 heat treated at 1700°F but greater than the level found in this material when it was heat treated at 1800°F. Several other examples of the presence of this "phase" are shown in Figure 19. Heat 1357A with very low nitrogen showed the thickest boundary areas. Heat 1310A which contained low carbon as well as low nitrogen formed thick boundary regions and massive particles of sigma phase during testing at 1200°F after heat treatment at 1750°F. This behavior was similar to the behavior of the alloy after heat treatment at 1950°F. The boundary thickness after testing at 1200°F of Heats 1341A, 1338B and 1339A, each having high nitrogen, was greater after 1750°F heat treatment than after heat treatment at 2050°F, but it was not as great as in low nitrogen heats which had similar histories. The boundaries in the heat with high nitrogen and low carbon (Heat 1343A; 0.145%N and 0.02%C) were only slightly thicker after testing following heat treatment at 1750°F than when tested after heat treatment at 2050°F. These results imply that carbon was responsible for a greater variance in the grain boundary characteristics of the specimens after testing at 1200°F than was nitrogen. The variations related to the carbon content can be lessened, however, if nitrogen is simultaneously present. These microstructural

effects are very likely related to the tendency for sigma phase formation. This will be discussed further in a following section.

Fracture Characteristics. As another part of the microscopic examination of the alloys, the characteristics of the cracks found in the fractured specimens were studied. Two types of cracks could generally be found: (a) "Wedge" cracks, which usually initiated at a three grain junction and subsequently spread along the boundaries, and (b) "Cavity" type cracks, where numerous small cavities formed along the grain boundaries, grew and linked up, to cause eventual fracture. [12] The significant fracture characteristics of the specimens tested in this investigation can be summarized as follows:

(a) Heats with very low carbon and nitrogen exhibited a ductile, transgranular fracture.

(b) Most other heats had both wedge and cavitation type cracks after testing. "Wedge" cracks formed if carbon was the primary strengthener while "cavitation" type cracks formed if nitrogen was the primary strengthening element. In addition, the specimens heat treated at lower temperatures (1750°F) tended to have fewer cracks. The cracks which were present tended to be of the cavitation type. Numerous authors [13, 14, 15, 16] have shown that thin, often continuous, films of carbide precipitate form at grain boundaries of Type 304 steel at 1200°F. These films probably aided the formation of the wedge cracks. Decreasing the carbon content, or otherwise suppressing the formation of the grain boundary carbide films, should decrease the extent of the wedge cracking.

(c) The alloy to which no manganese was added exhibited a significantly different type of fracture from these heats which contained manganese. This heat (Heat 1340) had relatively low ductility and exhibited extensive wedge cracks throughout the gage section.

Precipitate Identification. Some further microstructural data were obtained using other techniques. Electron micrographs of some of the minor microconstituents present in extraction residues are shown in Figure 20. These constituents were identified by selected area electron diffraction.

The triangular particles in Figure 20a, b and c, identified as $M_{23}C_6$, were found in all specimens except those with very low carbon content. This type of carbide precipitate has been commonly observed [13, 14] and is generally believed to form at twin and grain boundaries. The bead-like $M_{23}C_6$ particles in Figure 20e were formed together with the triangular particles. Figure 20d shows a grid-like set of particles from a specimen from Heat 1339A which may be M_6C rather than $M_{23}C_6$. Kinzel [13] described these particles as forming at twin ends. In addition, several small irregular particles were also found in this specimen and these particles appeared to be M_6C.

It should be noted that the $M_{23}C_6$ and M_6C carbides are both face-centered cubic and have lattice parameters which vary between 10 and 11Å with the parameter of M_6C being slightly larger. For this reason it was very difficult to distinguish between these two phases using ordinary selected area electron diffraction techniques.

The only specimen studied which had a very low carbon content also had a very high nitrogen content (0.23%). The particles shown in Figure 20f and 20g are from this material (Heat 1343B). No pattern could be obtained from the particles shown in Figure 21g and, unfortunately, the particles in Figure 20f were not positively identified. The elctron diffraction pattern from the particles shown in Figure 20f exhibited two forms, one pattern being diffracted normal to the $\begin{bmatrix}100\end{bmatrix}$ cube direction and one normal to the $\begin{bmatrix}110\end{bmatrix}$ direction. The $\underline{d}$ values indicate that both patterns were from the same compound. This compound was cubic and had a lattice parameter of $\underline{a}$ = 5.7Å. No likely compound fitting this pattern was found in the ASTM Card File.

Ferrite. During the course of the microstructural investigation, the ferrite content of various cold worked materials was measured using an Aminco-Brenner Magne-Gage. The calibration curve used was essentially that developed by Simpkinson and Lavigne. [17] The ferrite content was measured on samples which had been heat treated at 2050°F and in some instances 1750°F, prior to cold working. These data are tabulated in Table VI. The results of this study are as follows:

(a) Increasing amounts of cold working resulted in the formation of increasing amounts of ferrite.

(b) Increasing "purity" of the alloy resulted in increasing amounts of ferrite at all levels of cold work. With similar amounts of cold work the ferrite content of Heat 1310A with neither carbon nor nitrogen was much greater than that of Heat 1318 with 0.096 percent carbon or Heat 1343A with 0.14 percent nitrogen or Heat 1341A with 0.06 percent carbon and 0.86 percent nitrogen.

(c) The production tubes PT-8 and PT-9 showed essentially no ferrite, even after severe deformation. The high austenite stability of the commercial tube PT-9 is most probably due to the high nitrogen content of this heat *. The high stability of tube PT-8 is also taken as being indicative of a high nitrogen level. (The great austenite stabilizing power of nitrogen is well documented in the literature, see, for example, Ref. 4, 18, 19, 22, 23, 24, 25.) Tubes PT-10 and PT-11 with lower nitrogen levels, but otherwise similar compositions, did become unstable under cold deformation and some ferrite was observed to have formed.

(d) Specimens that contained ferrite prior to testing, whether the result of cold working or not, contained no magnetic phase after creep-rupture testing at 1200°F. This implies that the ferrite was converted to sigma phase and/or austenite during testing.

* The slightly greater austenite stability of the commercial heats over the laboratory heats of similar nitrogen and carbon content is most likely due to the somewhat greater homogeneity of the commercial material.

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Recrystallization. In the investigation by White and Freeman[1] it appeared that not all of the Type 304 material had recrystallized during heat treatment for ½ hour at 1750°F. This, it was suggested, might be related to the low strength of the material after 1750°F heat treatment. To check this possibility, the recrystallization characteristics of Type 304 steel were re-examined; a detailed description of this study is presented in Appendix B. The following observations were made:

(a) Cold reductions of 45 and 25 percent were sufficient to give a completely recrystallized grain structure after ½ hour at 1600°F and 1750°F respectively. The low rupture strength at 1200°F after 1750°F heat treatments of material treated in this way cannot be attributed to lack of recrystallization since all material tested had recrystallized prior to testing.

(b) Precipitation of chromium carbides could precede recrystallization at temperatures from 1400° to 1750°F. This precipitation occurs on the original cold worked structure and can mask the actual recrystallized structure (this, of course, is dependent on metallographic technique). This type of precipitation prior to recrystallization has not been observed in Type 321 steel. [1] The reason for this difference between the two steels is not presently understood.

(c) Carbide precipitation either before or after recrystallization had a restrictive influence on grain growth.

(d) It was further observed that specimens cold worked 45 percent could undergo recrystallization in times between 50 and 500 hours at 1200°F. At 1200°F, recrystallization apparently aided the formation of sigma phase. This is similar to the phenomenon reported by Lena and Curry[26] in Type 310 steel.

DISCUSSION

In order to achieve the objectives of this program the experimental investigation focussed on the influence of variations in chemical composition and heat treatment. The metallurgical implications of these results need to be discussed prior to general discussion of how the results relate to the objectives of the program.

Carbon and Nitrogen

The creep-rupture properties of Type 304 austenitic steel were found to be extremely dependent on the concentration of the interstitial elements carbon and nitrogen.

Increasing the carbon content of Type 304 steel resulted in increased creep-rupture strengths. The strengthening effect gained by increased carbon content was limited by the solubility of the carbide phases at the heat treating temperature. The carbon solubility of Type 304 steel is shown in Figure 21.[27] The carbon solubility curve for Type 321 steel[2] is also shown for comparison. From Figure 21 it can be seen that the limit of carbon solubility at 1750°F is about 0.05 percent while between 1950° and 2050°F the solubility of this element is 0.09 and 0.11 percent. These values correspond within experimental error to the changes in the 1000-hour rupture strength as a function of temperature of heat treatment which were shown in Figure 1.

The above statements indicate that there is a relation between carbon content and heat treatment temperature for Type 304 steel similar to the "minimum temperature of heat treatment for maximum strength" relation that White[1, 2] found for Type 321 steel. This relation appears to hold so long as no precipitation occurred during the heat treatment. The influence of carbon in Type 304 steel was not nearly as strong as was observed in Type 321 steel (where increasing carbon content in solution led to the formation of increasing amounts of TiC during testing) and can probably be accounted for by the weaker chromium-carbon interactions and/or solution effects. The correlation presented for Type 321 steel[2] did not indicate a limit to the amount of strengthening within the range com-

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positions reported. Again this is probably related to the strength of the interaction resulting in compound formation. The lack of a significant difference between the rupture strengths of the high carbon Type 304 material after 1950° and 2050°F heat treatments suggests that there may be some other limitation on the influence of carbon in this alloy.

The strengthening due to nitrogen is somewhat greater on a weight basis that that due to carbon; on an atomic basis the relative effect is even greater. Other authors have also shown that nitrogen can have a potent strengthening effect on the creep-rupture properties of Type 304 steel. [7, 19, 28, 29, 30] The amount of nitrogen strengthening is probably limited by the solubility of nitrogen in the alloy. The solubility limit of nitrogen however, appears to be greater than that of carbon* (this was also suggested by Hum and Grant[19] and Brady[28]). The greater solubility of nitrogen compared with carbon is particularly evident after low temperature heat treatment. The rupture properties of the nitrogen strengthened alloy were only slightly lower after the 1750°F heat treatment than after the 2050°F treatment. This was in marked contrast to the behavior of alloys containing carbon.

The data suggest that the strengthening influence of carbon and nitrogen is partly attributable to solution effects such as atmosphere formation. These types of phenomena have been described extensively in the literature.[2] In the case of carbon, atmosphere formation is indicated by the strain aging observed in tensile tests at 1200°F.[2] The observation that carbides do not appear within the grains until extended exposure times have elapsed

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* Unlike the situation in the case of carbon, the survey of the literature failed to uncover the solubility data for nitrogen in 18Cr - 10Ni type alloys over the desired temperature range. However, there are data available for related alloys and for various alloys in the nolten state (18, 31, 32, 33, 34). Studies of other alloys containing nitrogen shed some light on the extent of solubility of nitrogen at lower temperatures (20, 24, 25, 28, 35, 36). From the various data it is suggested that at 1900°F the solubility of nitrogen in Type 304 austenitic steel is at least 0.20 percent and increased with increasing temperature. At lower temperatures the solubility of nitrogen is less certain but it may well be in excess of 0.05 percent at 1200°F.

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indicates that solution effects are operative. This was even more evident in the case of nitrogen. Since no evidence of precipitation was found, even after very long exposures, the conclusion must be reached that the strengthening effect of nitrogen did not rely on a precipitation mechanism.

Thus at 1200°F the strength of single phased Type 304 was apparently governed by the amount of carbon and nitrogen in solution. This behavior has also been found in Cr-Mn-C-N steels. [21] The mechanism is probably related to the dragging of atmospheres by dislocations or the pinning of dislocations rathern than the microscopic compound precipitation.

The behavior of the carbon bearing heats during testing after low temperature heat treatment has been shown to be quite different from the behavior exhibited after high temperature heat treatment. The differences in properties at 1200°F after various heat treatments point up the differences between the strengthening effects due to carbon and to nitrogen. The suggestions of the data as to the factors which control the properties of the heats after low temperature heat treatment are as follows:

(a) The low strengths resulting from low temperature heat treatment cannot be attributed to lack of recrystallization. All the Type 304 specimens treated at 1750°F and the commercial tube treated at 1600°F had recrystallized prior to testing.

(b) In materials containing carbon in excess of the solubility limit at the heat treating temperature, carbide precipitation occurred to some extent on the cold worked structure and at the grain boundaries of the newly recrystallized grains. This had the effect of restricting grain growth.

(c) The low temperature heat treatment reduced the carbon content of the matrix. This was made evident by carbide precipitation prior to testing and by the generally precipitate-free, deformed grains (characteristic of low carbon, low nitrogen heats) observed after testing materials containing carbon and very low nitrogen. In the heats containing nitrogen the grains were generally free of carbide precipitate but they were not greatly deformed, indicating that significant amounts

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of nitrogen were not removed from the grains by heat treatment at 1750°F.

(d) After 1750°F heat treatment, the 1000 hour rupture strengths of the heats shown in Figure 1 with carbon contents above the solubility limit at that temperature and of Heat 1341A (0.06%C, 0.08%N) were reduced to a level characteristic of material with only about 0.02 percent carbon, rather than that characteristic of material with 0.05 percent carbon, which is the solubility limit of carbon at 1750°F.

(e) Low temperature heat treatment did not appreciably alter the properties of Heat 1343A, which had very low carbon but high nitrogen.

(f) The decrease in the number of wedge cracks in rupture specimens subjected to a 1750°F heat treatment is probably indicative of a change in the predominant type of carbide precipitate at the boundaries.

(g) Low temperature heat treatment of carbon bearing heats resulted in the formation of more sigma phase during testing at 1200°F than did higher temperature heat treatments.

(h) The more extensive sigma phase formation was accompanied by more extensive "boundary thickening".

It would appear from the above statements that one or more distinct phenomena may be limiting the rupture strength at 1200°F of the alloys with carbon contents above 0.06 percent after heat treatment at 1750°F. The following possibilities should be considered:

(a) The carbide phases precipitated at the grain boundaries during the heat treatment had a deleterious effect on strength. This is suggested because such carbide precipitation occurred in all the cases where the strength was adversely affected by heat treatments at the lower temperatures. However, there appears to be no known mechanism whereby the results of both the carbon and carbon-nitrogen heats can be accounted for using the amount and type of carbide precipitation at the boundaries as the strength-limiting factor.

(b) The grain boundary depletion of chromium resulting from sigma phase

and/or carbide formation resulted in inherently weak material which limited the strength of the alloy. First, this form of sigma phase precipitate should not have an adverse influence on rupture properties. Secondly, the only basis for proposing that the chromium depleted region should be inherently weaker than the matrix would be that the level of carbon and particularly the level of nitrogen was lower in this region. This latter effect may be tenable, but little support for it can be offered. Furthermore, this would suggest that the deleterious effect would be decreased if the boundary thickening were decreased. Such a case is found in Heat 1341A, where the nitrogen apparently suppressed sigma phase formation and boundary thickening, but the loss of strength was still large. Thus there seems to be no correlation between the boundary depletion phenomenon and high temperature properties.

(c) Restricted grain growth due to precipitation may be responsible for low strength. If this is the case, the actual mechansim would probably be something other than simply a grain size effect since grain size itself has been shown to have little influence on properties. [37]

(d) Carbon and nitrogen in solution may be the controlling factors as in the case of the high temperature heat treatments. The carbon content of the matrix, however, may be reduced below the solubility limit at the temperature of heat treatment by some other mechanism. This might be due to heterogeneous carbon distribution or to some precipitation phenomena. Such a reduction of the carbon level in the matrix to about 0.02 percent in an alloy containing 0.06 percent carbon or more would adequately account for the observed results.

The factors limiting the strength of Type 304 steel after low temperature heat treatment are not as clearly defined as those governing the behavior of the material after high temperature heat treatment. The factor controlling the strength may be the carbon and/or nitrogen content of the solution and this may be adversely affected by a precipitation phen-

omenon during heat treatment.

One further comment is in order in regard to Type 304L steel. This material has low carbon content (0.035% maximum) in order to prevent carbide precipitation at grain boundaries which may lead to susceptibility to intergranular corrosion.[13, 14] It has been observed that nitrogen in Type 304 steels does not contribute as significantly to the process of intergranular corrosion as does carbon.[22, 28] This may be due to the greater solubility of nitrogen or a difference in the nature of the compounds which precipitate. Thus it would appear that Type 304L steel with high nitrogen levels could have nearly the same strength as Type 304 steel. This has been verified by Brady.[28]

Titanium and Boron

To this point the discussion has centered around heats with carbon and nitrogen additions. Some further discussion is in order relating to the influence of titanium and boron on the strength of the steel.

Additions of small amounts of titanium were made to different heats to investigate any influence which very "reactive" elements might have on the properties of Type 304 steel. The results, stated previously, showed that in the absence of nitrogen the addition of about 0.03 percent titanium resulted in an increased 1000-hour rupture strength, the extent of this increase being dependent on the carbon level of the alloy. In heats containing nitrogen the 1000-hour rupture strength was decreased from 24,000 to 22,000 psi by the addition of 0.03 percent titanium. Nowak[8] has reported titanium to have a deleterious effect on the rupture strength at 1200°F of Type 304L steel. He attributed the reduced properties to TiN formation. Kozlik[38] in reporting on Type 304L has also shown an effect of titanium on the properties of the steel which can be attributed to titanium combining with nitrogen to form TiN.

In the heats containing titanium and nitrogen, numerous TiN particles were observed throughout the structure. These were not put into solution

during the heat treatment at 2050°F. This confirms that the loss in strength of the steel is due to nitrogen tie-up by titanium. In addition, the removal of nitrogen (or carbon) by titanium would favor more sigma phase formation which in turn would give rise to more depletion of chromium around the boundaries. This also was observed.

From Figure 2 it can be seen that the loss in 1000-hour rupture strength of 2000 to 3000 psi would require the tying-up of about 0.02 to 0.04 percent nitrogen. For this amount of nitrogen to be tied up as TiN, 0.06 to 0.14 percent titanium would be require. Thus it would appear that the loss in strength is greater than might be attributed to nitrogen tie-up by 0.03 percent titanium. The change in the slope of the stress-rupture time curve of Heat 1344B may also imply that something more is involved than simply nitrogen removal. The data, however, are not sufficiently clear to draw any conclusion other than that titanium can decrease the rupture strength of Type 304 by combining with and tying up nitrogen. When no nitrogen is present, or if the nitrogen is completely "tied up", titanium can strengthen Type 304 steel slightly through an interaction with carbon.

Despite the efforts of many investigators the mechanisms of the effects which are attributed to boron are not understood. The results found in this investigation indicate that small additions of boron (15 ppm) can be very beneficial if compound formation (other than borides) is actively involved. The addition of boron to heats containing carbon, nitrogen or titanium had only minor effect, however, similar additions to heats containing titanium and either carbon or nitrogen resulted in significant increases in the stress-rupture properties. The benefit derived from such additions was usually greatest in the shorter time (high stress) rupture tests with diminished effectiveness at long times (see Figure 6).

The suggestion that the predominant effects of boron are associated with compound precipitation implies that boron alters the thermodynamic activities of some elements which are involved in compound forming reactions. The activity change might produce a change in the nature of the compound precipitated, the kinetics of the precipitation, or the size

and/or distribution of the precipitate. The latter effect has recently been observed in Type 321 steel by Crussard et al [39] and has previously been reported for other alloy systems. [40, 41] An alternative proposal [39] has been made in which it is suggested that boron markedly lowers grain boundary diffusion and consequently alters the precipitate distribution within the alloy. Although these proposals are not entirely adequate, they do appear to show the indirect manner in which boron is effective.

Thermodynamic Considerations

In order to tie together some of the effects found for the various alloy additions made to the laboratory heats and to provide a basis for the prediction of the possible effects of other elements, it is necessary to introduce thermodynamic data on compound formation.

In general, thermodynamic considerations of compound precipitation must be based on free energy data and the thermodynamic activities of the species involved. The latter data, however, are not available. Some conclusions may be drawn by considering similar cases and comparing the standard free energy of formation of various compounds. These data are available and several values are given below:

Standard Free Energy of Formation of some Carbides and Nitrides at 1200°F, BTU/pound mole of C or N (Ref. 42)

TiC	- 75,000	TiN	- 216,000	Cr_2N	- 48,000
CbC	- (50,000)	AlN	- 195,000	CrN	- 38,000
VC	- 35,000	CbN	- 135,000	Mo_2N	- 12,000
$Cr_{23}C_6$	- 33,000	Si_3N	- 95,000		
Al_4C_3	- 22,000	VN	- 85,000		
Mo_2C*	- 17,000				

* In contrast with the other metallic carbides and nitrides, the standard free energy of molybdenum carbides decreases with increasing temperatures (i.e. they become more stable).

From these considerations the following conclusions are suggested:

(a) TiN should form preferentially to and be more stable than TiC.

(b) Small amounts of aluminum should not react with carbon, however, aluminum should behave about like titanium with nitrogen.

(c) The free energies of the chromium carbides and chromium nitrides are of the same order of magnitude and without further thermodynamic data it would be difficult to conclude which should form first. Even allowing for the high concentration of chromium as compared with the other elements which are present in "trace" amounts, the driving force for the formation of the chromium compounds may be significantly lower than that of many other compounds.

(d) As vanadium is known to behave less ideally than silicon in solution it might be expected to form compounds preferentially to silicon. Judging from the free energies of formation listed previously, vanadium might be expected to behave with nitrogen as titanium does with carbon.

(e) The free energy data also indicate that molybdenum by itself should not be an active compound former in the residual amounts such as are present in Type 304 steel.

The above conclusions, despite their rather qualitative nature, show reasonable correspondence to the behavior of the elements added to the various heats. The following results for materials heat treated at 2050°F correspond closely with conclusions drawn from thermodynamic considerations: (1) The strengthening of the alloy realized by additions of carbon and titanium, (2) the decrease in strength noted when titanium or aluminum and nitrogen were present simultaneously, and (3) the lack of any effect due to the presence of aluminum with carbon. In addition the frequency of the formation of chromium carbides and nitrides is adequately predicted by the free energy data. There is no data available on the effect of columbium and nitrogen on the strength of Type 304, but there is evidence that they combine readily to form CbN. [43, 44] Columbium

is known to behave with carbon similarly to titanium. The creep and rupture data and the metallographic information suggest that the influence of molybdenum is primarily due to solid solution effects. This is consistent with the thermodynamic consideration. As far as vanadium is concerned, Nakagawa and Otoguro [45] have recently reported on its behavior in a carbon bearing 18Cr - 12Ni alloy and their results showed it to behave similarly to titanium. They further indicated that small amounts of vanadium and nitrogen can be put into solid solution. Hull et al [46, 47] has recently observed that small precipitates of VN_x were formed in Kromarc 58 steel. These precipitates were throught to be partly responsible for the strengthening of that steel. Kromarc 58 is not directly comparable with Type 304 steel, the former being a 16Cr - 20Ni - 10Mn - 2Mo base alloy, however, the precipitation of VN_x during creep in Kromarc 58 in a manner similar to that suggested by White [2] for TiC in Type 321 steel, tends to confirm the suggested thermodynamic similarity between the vanadium/nitrogen and titanium/carbon interactions.

In addition, this combination of thermodynamic-mechanistic reasoning suggests that strong interactions like that of titanium / carbon may be most potent in short time periods, but that milder interactions may be more effective strengtheners over longer time periods. It appears possible that the stronger the interaction, the more rapidly its beneficial effects may become mitigated due to precipitation. This suggestion is to some degree borne out in the discussion in the following section. Further mechanistic speculation seems unwarranted at this point. There is in the literature a general discussion of various aspects of such mechisms (see Refs. 2, 48, 49, 50).

The primary conclusion to be drawn from these considerations is simply that the "reactivity" of an added element can provide some index of its behavior in Type 304 steel and how its behavior might subsequently influence the creep and rupture properties of the steel. This is based on the assumption that the creep and rupture properties of Type 304 steel are

primarily affected by carbon and nitrogen in solution, as well as the inter-actions of these and other elements in solid solution and the precipitation of compounds at dislocations. The predictions are necessarily qualitative but they provide the only way other than intuition of anticipating possible effects of other trace elements.

Long Time Properties

The 1000-hour rupture strength has been frequently used for comparison of the alloys studied in this investigation. For most tubing applications, however, the properties at much longer times are of primary interest. For many of the heats used in this investigation the rupture data at 1200°F was sufficient to establish approximate long-time properties. For certain heats data were obtained at 1350°F which were also used in the estimation of the long-time strength. These data have been used to construct the Miller-Larson diagram shown in Figure 22. There are two features of this figure that are of particular significance. First, the curves for the carbon and/or nitrogen-containing materials tested at 1200°F and 1350°F "fitted" together smoothly and had similar slopes. This behavior was also observed in the data of Brady [28] and suggests that a linear extrapolation of the 1200°F data to longer times is justified. Other investigators have confirmed the applicability of such an extrapolation. [51, 52] Second, the high strength of Heat 1339A (0.07%C, 0.124%N, 0.032%Ti, 15 ppm B) in comparison with the other heats is not maintained at long times.

The trend exhibited by Heat 1339A is suggestive of the findings reported for Types 321 and 347 steels. The short time rupture strength of these stabilized steels is significantly greater than that of Types 304 and 316 steels. The slopes of the rupture curves are greater, however, so that the 100,000-hour rupture strength of the unstabilized steels can be as high or possibly higher than that of the stabilized types. [1, 51, 52]

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"Old" versus "Modern" Material

The metallurgical variables which have been shown to be primarily responsible for the fluctuations in the high temperature properties of Type 304 steel have been discussed in the previous sections. It is now appropriate to consider the implications of the findings in terms of commercial practice and to attempt to use the findings to explain why Type 304 steel made during and prior to the early 1950's was generally weaker than currently produced material. (These materials will hereafter be referred to as the "old" and the "modern" steel.) Because of the lack of "old" Type 304 material for study in this investigation this latter explanation will necessarily be speculative.

Assuming that the thermo-mechanical treatments of the material were "adequate" or at least similar for both "old" and "modern" Type 304 alloy, there appear to be two main areas which should be considered as possible sources of variations in creep-rupture properties. These areas center around the influence of nitrogen and the influence of certain residual elements. Several mechanisms will be considered through which these elements can cause significant property variations in the alloy.

Higher effective nitrogen contents of "modern" steel could very well be responsible for its superior properties as compared with those of the "old" steel. The commercial tube material, PT-9, was studied in this investigation because of the high strength reported for it in the SP-6 investigation. [1] This tube was found to have 0.08 percent nitrogen. Its strength level corresponded very well with that predicted from Figure 2. Several other tubes from the same manufacturer were found to have nitrogen contents of the order of 0.10 percent. Nitrogen analyses from ten heats of Type 304L steel from another manufacturer range from 0.055 to 0.10 percent, averaging 0.078 percent nitrogen.* This level of nitrogen

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* These heats were quite similar in base composition and averaged 0.025%C, 1.32%Mn, 0.54%Si, 18.57%Cr and 9.31%Ni.

is considerably higher than the expected level of 0.02-0.05 percent. This lower nitrogen level is apparently characteristic of the "old" material. In most cases the nitrogen contents of various commercial heats are not given, so that further comparisons are not possible. It does appear, however, that high nitrogen levels are possible (and, indeed, probable) as the result of "normal" present day commercial practice.

There seem to be several ways in which a change in nitrogen level between "old" and "modern" Type 304 steel could have come about:

(a) Melting practice. It should be recognized that a melt with a nitrogen content in the range of 0.02 to 0.05 percent is considerably under-saturated in nitrogen with respect to the air. [18, 31, 32, 33, 34] Thus nitrogen pick-up from the atmosphere is a very real possibility and has been observed in this work* and has been reported under various circumstances by other authors. [5, 53, 54, 55] There could be numerous ways in which melting practice could influence the nitrogen pick-up.

(b) Deoxidation practice. It seems clear from the results found here that the excessive use of deoxidizers, particularly aluminum, could have an adverse effect on the high temperature properties of the material by removing nitrogen from the melt, or tying it up as a nitride in the solidified ingot. However, rather large quantities of aluminum, above that required for deoxidation, would be required to tie up substantial amounts of nitrogen - one pound per ton (.05%Al) could tie up 0.025 percent nitrogen. Furthermore, aluminum is by no means a standard deoxidizer for stainless steels. Common commercial practice also uses silicon and manganese as deoxidizers, if, indeed, any deoxidizer is used at all. For these reasons one is not justified in attri-

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* As an example, the nitride added to Heat 1343A should have resulted in a nitrogen content of 0.067 max. This molten heat was exposed to an atmosphere of nitrogen under a pressure of ½ atm. for about ten minutes. The resulting analysis showed the presence of 0.145 percent nitrogen - a pick-up of about 0.08 percent in ten minutes.

buting to deoxidizers sufficient nitrogen removal to account for the difference in rupture properties between the "old" and the "modern" materials.

(c) Base composition. One of the more obvious differences between the "old" and the "modern" material is a change in the base composition. During the 1940's and early 1950's the composition of Type 304 steel was typically 18 percent chromium and 8 to 10 percent nickel with the manganese and silicon contents usually between 0.10 and 0.60 percent. (Material considered for high temperature service, however, rarely had less than 9 percent nickel.) Toward the 1960's the manganese content was increased to about 1.50 percent while the nickel was typically 10.0 to 10.5 percent. Various studies, particularly that of Monkman et al [30] have found that variations in the nickel content have only small effects on the creep-rupture properties of Type 304 steel. Similarly, it has been shown [6] that the change from 0.50 to 2.00 percent manganese has no appreciable effect on creep-rupture properties.* However, a study of the available data indicates that the lower strength commercial heats of Type 304 steel are invariably associated with nickel and manganese on the low side of the allowable range. While this correlation may be fortuitous, at least one aspect suggested by it should be considered further.

It is possible that the findings cited above which relate to laboratory heats may not properly reflect the effect of similar compositional changes in commercial practice. Specifically, these changes may result in considerable variations in the nitrogen content of the steel. First, the addition of manganese to the melt may bring in nitrogen [54] or it may increase the solubility of nitrogen in the melt. [32, 34, 58] In this connection it was

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* Note: "Elimination" of the manganese, i.e. reduction to less than 0.10 percent, was found to have a deleterious effect on the creep-rupture properties of Type 304 steel at 1200°F. This may also account for the differences in properties reported in this investigation and those of an earlier study. (19)

observed that the ingots of Heat 1340 with very low manganese (.10%) and with high nitrogen added to the melt evolved considerable gas during solidification. This was not observed in any other laboratory heat and thus suggests that the solid solubility of nitrogen was indeed lower in the low manganese heats than in those with approximately 1.50 percent manganese. Second, the compositional changes could alter the solidification mode of the ingot. Inspection of the Fe-Cr-Ni ternary system (Refs. 56 and 57) and estimates of the nitrogen solubility in the high temperature δ-ferrite phase (from Refs. 18, 20, 31, 32, 58) suggests that solidification through the δ-ferrite region, which would likely be in heats with low nickel and manganese, could result in a heat low in nitrogen content because of low solubility of nitrogen in δ-ferrite. A heat slightly richer in the austenite stabilizing elements could remain completely austenitic throughout solidification and have a high nitrogen content. Haefner et al [18] and Whittenberger et al [20] have shown that increasing manganese and nickel contents resulted in increased solid solubility of nitrogen. A difference in the austenite stabilizing elements (nickel and manganese) from 2.0 to 4.0 percent could conceivably change the nitrogen content of the material by as much as 0.10 percent. This could easily account for the differences in rupture strength between the "old" and "modern" material.

The results suggest that there may be other possible sources of differences in the properties. Various combinations of trace amounts of boron and/or other residual metallic elements such as titanium or columbium could affect the properties. The present data indicate that a substantial difference (probably greater than 0.03 percent) in residual content of titanium or columbium would be required to account for the difference in properties between the "old" and the modern" material. However, no evidence has been found that would suggest that the residual element content is different in the "old" and the "modern" material. The residual element content of four "modern" Type 304 materials is given in Table I; for "older" materials these data are not readily available. The few scattered data on various residual elements that were found* indicated that

* Ref. 104 and elsewhere

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the values in Table I are probably typical for the "old" material also. Considering that there have always been small variations between the practices of various manufacturers (both in regard to residual content and thermo-mechanical processing) it appears highly questionable whether these types of effects could be responsible for the consistent differences reported between the "old" and the "modern" materials.

While none of the above possibilities have actually been proven, they illustrate several ways in which differences in the creep-rupture properties could have come about. Changes in commercial practice which result in different nitrogen levels appear to be the most plausible explanation for the reported differences in the rupture properties of the "old" and the "modern" Type 304 steel.

CONCLUSIONS

The high temperature creep-rupture strength of Type 304 austenitic stainless steel, as currently produced commercially, is considerably greater than that of material made in the early 1950's and often of material made in the laboratory. In order to determine the reasons for these differences in strength level and to determine the factors controlling the high temperature strength of the alloy, this investigation has focussed principally on the influence of chemical composition and heat treating variables on the properties of Type 304 steel. The conclusions of the investigation pertaining to the factors controlling the high temperature properties of this alloy can be summarized as follows:

(a) The creep-rupture strength of Type 304 steel at 1200°F is primarily controlled by its carbon and nitrogen contents. Increasing amounts of these elements in solution prior to testing (or service) can impart increasing strength to the material. Carbon is a less potent strengthener than nitrogen and increases in carbon content beyond 0.10 per-

cent had no influence on rupture strength at 1200°F. Nitrogen is a very potent strengthener in Type 304 steel at levels up to at least 0.15 percent and possibly at higher levels.

(b) The role of various trace elements in Type 304 steel is determined by their "reactivity" with the carbon and nitrogen in solution in the alloy. Trace elements can have the following types of effects:

(1) A deleterious effect if the element is so reactive as to remove carbon or nitrogen from the solution prior to, or during, heat treatment (titanium has this effect with nitrogen).

(2) A beneficial effect if the element is moderately reactive with carbon and/or nitrogen, can be put into solid solution during heat treatment and can precipitate during subsequent testing (titanium has this effect with carbon and it is likely that vanadium would have this effect with nitrogen).

(3) No appreciable effect if the element is not reactive or is only weakly reactive with carbon or nitrogen in comparison with other elements present in the steel (molybdenum appears to be such an element).

In case (2) above, it was found that if the "reactivity" was moderately high the beneficial precipitation effect could be dissipated rather quickly so as to result in substantially improved short time properties but relatively unchanged long time properties (this appears to be the case with the titanium interaction with carbon).

(c) The influence of varying heat treatment temperature appears to be related to the solubility of the carbides and nitrides. The presence of relatively stable compounds required that higher heat treating temperatures be used to achieve maximum strength. Excessively low heat treating temperatures (1750°F) had a particularly harmful effect on alloys in which the carbon content was considerably above the solubility limit of carbon at the heat treating temperature; the strength of these materials was lower than the strength expected in a material whose carbon content was equal to the solubility limit at that temper-

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ature. The reason for this is not understood but it may be related to precipitation during heat treatment. A minimum temperature of heat treatment of 1800°F for cold worked material appears to develop maximum or near maximum high temperature properties in material with normal carbon contents.

(d) Heats with high nitrogen levels (around 0.10%) and very low manganese levels (around 0.10%) have very low rupture ductility and low creep-rupture strength at 1200°F.

These findings, together with available high temperature property data and the known variations in chemical composition and in thermo-mechanical processing that are possible in commercial practice allow the following conclusions relative to the difference in properties between the "old" and "modern" Type 304 steel:

(a) The difference in high temperature properties between the "old" and "modern" material cannot be attributed to the effects of trace elements.

(b) Differences in nitrogen content between the "old" and the "modern" material can account for the observed differences. In the few commercial heats for which nitrogen analyses are available, there was a marked difference in nitrogen content, ranging from about 0.02 - 0.04 percent for the "old" material (averaging about 0.03%) to approximately 0.04 - 0.10 percent for the "modern" material (averaging about 0.08%).

(c) It is suggested that this difference in nitrogen has probably come about through changes in melting practices and/or the small compositional change of the metallic austenite stabilizing elements (manganese and nickel). The latter possibility would lead to increased nitrogen solubility and/or a change in the phase equilibrium during solidification, which might result in greater retention of nitrogen in the metal.

RECOMMENDATIONS

The findings of this investigation suggest that consideration of nitrogen in Type 304 steel in needed. This conclusion follows regardless of whether or not nitrogen is responsible for the differences between the "old" and the "modern" material, since it has been shown that nitrogen has a substantial influence on the creep-rupture properties of Type 304 austenitic steel at 1200°F.

The proper method of specifying nitrogen content is open to question. The approach which is suggested at the present time is to combine the carbon and nitrogen levels into a parameter, recognizing from Figures 1 and 2 that nitrogen is about 25 percent more potent than carbon in strengthening this alloy. Subject to certain qualifications it is thought that the parameter (%C) + 1.25 (%N), should be set equal to or greater than some minimum value. The primary qualification of the above statement is that the carbon and nitrogen must be in solution before the material is subjected to creep conditions.

Figure 23 was prepared to aid in the determination of a minimum value for the combined carbon and nitrogen level. This figure presents the extrapolated 100,000-hour rupture strength of all the "carbon-nitrogen" laboratory heats from this investigation and from that of White and Freeman [1] and data from the few commercially produced materials for which nitrogen analyses are available. Specific information pertaining to the commercial materials used in Figure 23 is given in Appendix C. It should be noted that these materials are similar in that they are all compositionally balanced so as to be wholly austenitic, however, the prior histories of the various materials differ considerably. If the basis for specifying carbon and nitrogen contents is taken as a minimum 100,000-hour rupture strength of 8,500 psi, then from Figure 23 a minimum value for (%C) + 1.25 (%N) of 0.13 would appear to be appropriate.

Because of the importance of a criteria such as discussed above and because the correlation from which it is derived is based on only limited

commercially produced material, it is strongly recommended that its acceptance be dependent upon further verification. This might be accomplished by providing nitrogen analyses for materials for which elevated temperature data presently exist.

Based on the discussion of the differences between the "old" and the "modern" material, it is possible that low nickel (8.0 - 9.0 percent) and manganese (0.10 - 0.60 percent) levels may adversely affect the solubility of nitrogen and its retention on solidification. Although material with these levels of manganese and nickel is not used for seamless superheater tubing applications, it is allowed by the present ASTM standards, (A-312, A-376, A-213) which cover this material. Therefore it is recommended that Type 304 material selected for high temperature seamless tube applications have nickel and manganese levels comparable to those of the currently produced material, i.e. 9.0 - 11.0 percent nickel and 1.0 - 2.0 percent manganese. These levels of nickel and manganese should provide adequate nitrogen solid solubility in the steel so that the desired high strength level can be achieved.

REFERENCES

1. White, J. E. and J. W. Freeman: "Metallurgical Principles Governing The Creep-Rupture Strength of Type 321 Austenitic Steel Superheater Tubing with Limited Extension to Type 304 and Type 316 Austenitic Steels", Trans. ASME, Vol. 85, Series A, p. 119, 1963.

2. White, J. E. and J. W. Freeman: "A Study Designed to Explain the Creep-Rupture Strength of Type 321 Superheater Tubing", Trans. ASME, Vol. 85, Series A, p. 108, 1963.

3. Adcock, F: "The Effect of Nitrogen on some Chromium and some Iron-Chromium Alloys", Journal of the Iron and Steel Institute", p. 117, 1926.

4. Uhlig, H. H.: "The Role of Nitrogen in 18-8 Stainless Steel", Trans. ASM, Vol. 30, p. 947, 1942.

5. Gluck, J. V. and J. W. Freeman: "Effect of Creep-Exposure on Mechanical Properties of Rene' 41. Structural Studies, Surface Effects and Re-Heat Treatment", ASD Technical Report, 61-73 Part II.

6. Timken Roller Bearing Company: Resume' of Investigations on Steels for High Temperature, High Pressure Applications, 1960-1962.

7. Nakagawa, R. and Y. Otoguro: "The Effects of Nitrogen and Boron on Properties of 18 Chromium-12 Nickel Stainless Steels", Trans. NRIM, Vol. 5, p. 129, 1963.

8. Nowak, C.: "Trace Elements in Type 304 Stainless Steel", Private communication, March 5, 1964.

9. Nakagawa, R. and Y. Otoguro: "Effects of Molybdenum on Properties of 18 Chromium-12 Nickel Austenitic Stainless Steels", Trans. NRIM, Vol. 3, p. 99, 1961.

10. Dulis, E. J. and G. V. Smith: "Identification and Mode of Formation and Re-Solution of Sigma Phase in Austenitic Chromium-Nickel Steels", ASTM STP No. 110, Symposium on Sigma Phase.

11. Gilman, J. J.: "Electrolytic Etching - The Sigma Phase Steels", Trans. ASM, Vol. 44, p. 566, 1952.

12. Low J. R., Jr.: "The Fracture of Metals", Progress in Materials Science, Vol. 12, 1963, Pergamon Press.

13. Kinzel, A. B.: "Chromium Carbide in Stainless Steel", Trans. AIME, Vol. 194, p. 469, 1952.

14. Stickler, R. and A. Vinckier: "Morphology of Grain Boundary Carbides and Its Influence on Intergranular Corrosion of 304 Stainless Steel", Trans. ASM, Vol. 54, p. 362, 1961.

15. Stickler, R. and A. Vinckier: "Morphology of Grain Boundary Carbides in a 304 Stainless Steel", Acta. Met., Vol. 9., Letter to the Editor P. 898, 1961.

16. Stickler, R. and A. Vinckier: "Precipitation of Chromium Carbide on Grain Boundaries in a 302 Austenitic Stainless Steel", Trans. AIME, Vol. 224, p. 1021 1962.

17. Simpkinson, J. V. and M. J. Lavigne: "Detection of Ferrite by its Magnetism", Metal Progress, Vol. 55, No. 2, p. 164, Feb. 1949.

18. Haefner, K., A. F. Lahr, W. L. Meinhart and J. J. Kanter: "Property Relationships of Some Cast and Forges Cr-Mn-Ni-N Steels Containing 18 Per Cent Chromium", Trans. ASTM, Vol. 59, p. 804, 1959.

19. Hum, J. K. Y. and N. J. Grant: "Austenite Stability and Creep-Rupture Properties of 18-8 Stainless Steel", Trans. ASM, Vol. 45, p. 105, 1953.

20. Whittenberger, E. J., E. R. Rosenon and D. J. Carney: "Phase Relations in Cr-Ni-Mn-N Steels Above 2100°F", Trans. AIME, Vol. 209, p. 889, 1957.

21. Kasak, A., C. M. Hsiao and E. J. Dulis: "Relationships Between Composition and Properties of Austenitic Chromium-Manganese-Carbon-Nitrogen Stainless Steels", Trans. ASTM, Vol. 59, p. 786, 1959.

22. Franks, R., W. D. Binder and T. Thompson: "Austenitic Chromium-Manganese-Nickel Steels Containing Nitrogen", Trans. ASM, Vol. 47, p. 231, 1955.

23. Rudorff, D. W.: "Nitrogen as an Alloying Element in Cr-Ni Steels", Metallurgica, Vol. 27, p. 68, 1942.

24. Tisinai, G. F., J. K. Stanley and C. H. Samans: "Austenitic Fe-Cr-C-N Stainless Steels", Trans. ASM, Vol. 48, p. 356, 1956.

25. Tisinai, G. F. and C. H. Samans: "Phase Relations in the Fe-Cr-Ni-N System", Trans. ASM, Vol. 51, p. 589, 1959.

26. Lena, A. J. and W. E. Curry: "The Effect of Cold Work and Recrystallization on the Formation of the Sigma Phase in Highly Stable Austenitic Stainless Steels", Trans. ASM, Vol. 47, p. 193, 1955.

27. Rosenberg, S. J. and C. R. Irish: "Solubility of Carbon in 18-Percent Chromium-10-Percent Nickel Austenite", Journal of Research of the National Bureau of Standards, Vol. 48, p. 40, 1952.

28. Brady, R. R.: "AISI Type 304L Stainless Steel with Improved Strength", Trans. ASTM, Vol. 59, p. 774, 1959.

29. Dulis, E. J., G. V. Smith and E. G. Houston: "Creep and Rupture of Chromium-Nickel Austenitic Stainless Steels", Trans. ASM, Vol. 45, p. 42, 1953.

30. Monkman, F. C., P. E. Price and N. J. Grant: "The effect of composition and structure on the creep-rupture properties of 18-8 stainless steel", Trans. ASM, Vol. 48, p. 418, 1956.

31. Smithells, C. J., "Metals Reference Book", Third Edition, 1962, Butterworths Publishers.

32. Pehlke, R. D. and J. F. Elliott: "Solubility of Nitrogen in Liquid Iron Alloys", AIME, Vol. 218, p. 1038, 1960.

33. Humbert, J. C. and J. F. Elliott: "The Solubility of Nitrogen in Liquid Fe-Cr-Ni Alloys", Trans. AIME, Vol. 218, p. 1076, 1960.

34. Langenberg, F. C.: "Predicting the Solubility of Nitrogen in Molten Steels", Trans. AIME, Vol. 206, p. 1099, 1956.

35. Tisinai, G. F. and C. H. Samans: "Phase Relationships and Mechanical Properties of Some Fe-Cr-C-N Alloys", Trans. ASM, Vol. 49, p. 747, 1957.

36. Paranjpe, V. G., M. Cohen, M. B. Bever and C. F. Floe: "The Iron-Nitrogen System", Trans. AIME, Vol. 188, p. 261, 1950.

37. Freeman, J. W. and C. L. Clark: "The Apparent Influence of Grain Size on the High Temperature Properties of Austenitic Steels", Trans. ASM, Vol. 38, p. 148, 1947.

38. Kozlik, R. A.: "Developments in Alloys for High Temperature Service: Stainless Steel", International Nickel Co., Research Seminar, 1961.

39. Crussard, C., J. Plateau and G. Henry: "The Influence of Boron in Austenitic Alloys", Proceedings of the Joint International Conference on Creep, Paper 64, p. 1-91, 1963.

40. Decker, R. F. and J. W. Freeman: "The Mechanism of Beneficial Effects of Boron and Zirconium on Creep Properties of a Complex Heat-Resistant Alloy", Trans. AIME, Vol. 218, p. 277, 1960.

41. Levitin, V. V.: "Investigation of the Influence of Boron on the Decomposition of a Supersaturated Solid Solution at Grain Boundaries in Austenitic Steels", Physics of Metals and Metallography, Vol. 11, No. 3, p. 67, 1961.

42. Elliot, J. F. and M. Gleiser: "Thermochemistry for Steelmaking", Vol. 1, 1960, Addison-Wesley.

43. Rosenberg, S. J. and J. H. Darr: "Stabilization of Asutenitic Stainless Steels", Trans. ASM, Vol. 41, p. 1261, 1949.

44. Heeley, E. J., A. T. Little and D. F. Darbyshire: "Some observations on the niobium content required for stabilization of 18-8-Nb Steels", Journal of the Iron and Steel Institute, Vol. 200, p. 943, 1962.

45. Nakagawa, R. and Y. Otoguro: "The Effects of Vanadium on Properties of 18 Chromium-12 Nickel Austenitic Stainless Steels", Trans. NRIM, Vol. 4, p. 64, 1962.

46. Hull, F. C.: "A High-strength Weldable Stainless Steel for Elevated-Temperature Service", ASTM, Symposium on Advances in the Technology of Stainless Steel - Atlantic City, June 1963.

47. Hull, F. C. and R. Stickler: "Effects of N, B, Zr and V on the Microstructure, Tensile and Creep-Rupture Properties of a Cr-Ni-Mn-Mo Stainless Steel", Proceedings of the Joint International Conference on Creep, Paper 43, p. 1-49, 1963.

48. Irvine, K. J., J. D. Murray and F. B. Pickering: "The Effect of Heat Treatment and Microstructure on the High-Temperature Ductility of 18%Cr-12%Ni-1%Nb Steels", Journal of the Iron and Steel Institute, Vol. 196, p. 166, 1960.

49. Garofalo, F., F. von Gemmingen and W. F. Domis: "The Creep Behavior of an Austenitic Stainless Steel as Effected by Carbide Precipitation on Dislocations", Trans. ASM, Vol. 54, p. 430, 1961.

50. Myres, J.: "Hot Ductility of Three Austenitic Steels", British Welding Journal, Vol. 9, p. 106, 1962.

51. Krebs, T. M. and N. Soltys: "A Comparison of the Creep Rupture Strength of Austenitic Steels of the 18-8 Series", Joint International Conference on Creep, Paper 34, p. 6-21, 1963.

52. Murray, D. J. and R. J. Truman: "The High Temperature Properties of Cr-Ni-Nb and Cr-Ni-Mo Austenitic Steels", Joint International Conference on Creep, Paper 61, p. 5-55, 1963.

53. Smith, G. V., E. J. Dulis and E. G. Houston: "Creep and Rupture of Several Chromium-Nickel Stainless Steels", Trans. ASM, Vol. 42, p. 935, 1950.

54. Carney, D. J. and E. J. Whittenberger: Electric Furnace Steelmaking, Vol. 1, "Raw Materials" p. 175, AIME, 1962, Interscience Publishers.

55. Feild, A. L. and P. R. Gouwens: Electric Furnace Steelmaking, Vol. 1, "Melting of Stainless Steel", p. 325, AIME, 1962, Interscience Publishers.

56. American Society for Metals: "Metals Handbook", 1948.

57. Pugh, J. W. and J. D. Nisbet: "The Iron-Chromium-Nickel Ternary System", Trans. AIME, Vol. 188, p. 269, 1950.

58. Flinn, R. A.: "Fundamentals of Metal Castings", 1963, Addison-Wesley.

59. Simmons, W. F. and H. C. Cross: "The Elevated Temperature Properties of Stainless Steel", ASTM-STP, p. 124, 1952.

60. Grant, N. J., A. G. Buckling and W. Rowland: "Creep-Rupture Properties of Cold-Worked Type 347 Stainless Steel", Trans. ASM, Vol. 48, p. 446, 1956.

TABLE I

Chemical Composition of Four Type 304 Austenitic Steel, Seamless Tubes

Tube Number	Composition, weight percent							
	C	N	Mn	Si	Ni	Cr	Mo	Cu
PT-8	0.057	- -	1.19	0.60	10.44	18.35	0.13	0.15
PT-9	0.054	0.082	1.78	0.48	10.41	19.09	0.03	0.07
PT-10	0.06	0.028	1.35	0.09	10.50	18.45	0.13	0.11
PT-11	0.04	0.031	1.42	0.50	10.00	18.56	0.12	0.04

	P	S	B	Al	Zr	Ti	Cb	V
PT-8	0.027	0.010	<0.001	<0.005	<0.01	<0.01	0.020	0.012
PT-9	0.019	0.010	<0.001	0.020	<0.01	<0.01	0.019	0.010
PT-10	0.024	0.011	0.0013	<0.005	<0.01	<0.01	0.015	0.029
PT-11	0.027	0.015	<0.001	<0.005	<0.01	<0.01	0.017	0.012

TABLE II

Chemical Composition of Laboratory Heats

Heat Number	Chemical Composition, Weight Percent								
	C	N	Mn	Si	Ni	Cr	Ti	B (ppm)	Other
1336A	0.05	–	0.74	0.54	10.75	19.0	–	15	
1336B	0.05[a]		0.74[a]	0.54[a]	10.75[a]	19.15[a]	–	15	
1337A	0.06	–	1.50	0.50	10.5	18.5	0.03	15	
1338A	<0.02	–	1.50	0.50	10.5	18.6	0.03	15	
1338B	<0.02[a]	0.13	1.50	0.50	10.63[a]	18.70[a]	0.03	15	
1339A	0.07	0.124[a]	1.50	0.50	10.6	18.5	0.03	15	
1339B	0.07[a]	0.13	1.50	0.50	10.59[a]	18.45[a]	0.03	30	
1340A	0.01	(0.11)	0.08	0.50	11.25	18.5	–	–	
1340B	0.04[a]	(0.12)	0.08	0.50	11.25	18.5	–	–	
1341A	0.06	0.087[a]	1.50	0.50	10.5	18.5	–	–	
1341B	0.13[a]	0.09	1.50	0.50	10.5	18.5	–	–	
1342A	0.03[a]	0.10	1.60	0.50	10.50	18.7	–	–	
1342B	0.07[a]	0.11	1.59[a]	0.53[a]	10.51[a]	18.77[a]	–	–	
1343A	0.02	0.145[a]	1.50	0.50	10.5	18.5	–	–	
1343B	0.02[a]	0.23	1.50	0.50	10.5	18.5	–	–	
1344A	0.06	–	1.50	0.50	10.5	18.5	0.035	–	
1344B	0.06[a]	0.12	1.50	0.50	10.5	18.5	0.035[a]		
1344C	0.06	0.14	1.50	0.50	10.5	18.5	0.08	–	
1357A	0.05	–	1.50	0.50	10.5	18.5	–	–	
1357B	0.05	–	1.50	0.50	10.5	18.5	0.03	15	
1358A	<0.02[a]	0.12	1.50	0.50	10.5	18.5	–	–	.03 Al
1358B	0.06	0.13	1.54[a]	0.39[a]	10.17[a]	18.18[a]	–	–	.03 Al
1360A	0.08	–	1.50	0.50	10.5	18.5	–	–	.03 Al
1360B	0.08[a]	0.12	1.50	0.50	10.5	18.5	–	–	.03 Al
1361A	0.03[a]	0.051[a]	1.50	0.50	10.5	18.5	–	–	
1361B	0.03	0.06	1.56[a]	0.44[a]	10.10[a]	18.17[a]	0.03	15	
1362A	0.07[a]	0.09	1.50	0.50	10.5	18.5	–	–	
1362B	0.16[a]	0.13	1.50	0.50	10.5	18.5	0.025[a]	15	
1363A	0.02[a]	–	1.50	0.50	10.5	18.5	–	15	
1363B	0.02	0.12	1.50	0.50	10.5	18.5	–	15	
1364A	0.02[a]	–	1.50	0.50	10.5	18.5	0.03		
1364B	0.02	0.12	1.50	0.50	10.5	18.5	0.030[a]		

TABLE II   concluded

Heat Number	Chemical Composition, Weight Percent								
	C	N	Mn	Si	Ni	Cr	Ti	B (ppm)	Other
1365A	0.06	0.12	1.50	0.50	10.5	18.5	–	–	0.19 Cu
1365B	0.06[a]	0.13	1.50	0.50	10.5	18.5	–	–	0.20 Mo[a] +0.19 Cu[a]
1366A	0.06	–	0.8	0.50	10.5	18.5	–	15	
1366B	0.06[a]	0.12	0.81[a]	0.50	10.5	18.5	–	15	
From Ref. 1 and 6:									
1310A	0.009[a]	0.01	1.42	0.46	10.38	18.46			
1310B	0.009	0.008	1.10	0.46	12.96	17.02		2.00 Mo	
1311	0.022	–	1.47	0.48	10.36	18.08			
1281	0.06	–	0.44	0.46	10.59	18.62			
1282	0.064	–	1.48	0.46	10.47	18.78			
1229	0.083	–	1.50	0.71	12.63	17.78			
1318	0.096	–	1.59	0.48	10.54	18.09			
1312	0.141	–	1.60	0.42	10.54	18.05			
1309A	0.087	0.049	0.61	0.40	10.54	18.77			
1309B	0.090	0.046	2.06	0.47	10.06	18.46			

a - Actual value from commercial analyst. Other values are based
    on these values, the aim analysis, and melting experience.

TABLE III

Summary of Creep-Rupture Tests

Specimen No.	Heat Treatment °F	Test Temp. °F	Stress psi	Rupture Life hours	R. A. %	Elong. %	Min. Creep Rate %/hr.
Commercial tube, PT-9:							
PT9-1	2050	1200	28,000	133.1	28.0	20.4	0.069
PT9-2	2050	1200	22,000	1047.5	36.2	23.2	0.0087
PT9-7	2050	1350	20,000	20.1	43.7	33.1	
PT9-8	2050	1350	10,000	1803.3	28.5	24.6	
Laboratory heats:							
37A-1*	2050	1200	25,000	1593.2	18.9	9.6	0.00335
37A-2	2050	1200	30,000	369.5	23.9	11.0	0.01300
37A-3	2050	1200	35,000	123.4	28.6	13.2	0.06380
38A-1	2050	1200	20,000	111.1	75.0	59.5	
38A-2	2050	1200	24,000	23.1	66.4	50.5	
38A-3	2050	1200	15,000	1075.5	56.6	43.2	
38B-1	2050	1200	20,000	4321.1	32.4	18.4	0.00160
38B-2	2050	1200	30,000	486.5	33.3	22.6	0.01962
38B-3	2050	1200	40,000	33.7	45.0	24.8	0.4200
38B-4	1750	1200	30,000	131.3	47.4	31.7	0.1125
38B-5	1750	1200	24,000	665.0	46.1	37.4	0.01825
39A-1	2050	1200	25,000	1799.2	22.1	15.4	0.0033
39A-2	2050	1200	30,000	721.2	23.5	14.9	0.0091
39A-3	2050	1200	35,000	189.7	27.0	18.4	0.0756
39A-4	2300	1200	35,000	173.0	37.4	18.1	0.0656
39A-6	2050	1350	15,000	344.6	43.8	39.1	0.0210
39A-7	2050	1350	20,000	94.9	46.7	33.1	0.1500
39A-8	2050	1350	12,000	878.7	38.7	20.9	0.00405
39A-9	1750	1200	30,000	72.5	48.6	40.6	0.2740
39A-10	1750	1200	20,000	824.9	44.8	35.4	0.0187
39A-12	1850	1200	30,000	231.5	25.1	17.4	
39A-13	1950	1200	35,000	135.3	29.0	22.8	
39B-1	2050	1200	25,000	1629.2	19.6	11.7	0.0041
39B-2	2050	1200	35,000	104.3	26.0	16.4	
39B-3	2050	1200	30,000	443.3	21.9	14.5	

*The specimen numbers are based on the last digits of the heat numbers.

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TABLE III continued

Specimen No.	Heat Treatment °F	Test Temp. °F	Stress psi	Rupture Life hours	R. A. %	Elong. %	Min. Creep Rate %/hr.
40A-1	2050	1200	25,000	109.0	12.7	5.1	(0.080)
40A-2	2050	1200	20,000	381.0	8.7	6.1	0.00586
40A-3	2050	1200	15,000	2581.7	4.9	4.7	0.00088
40B-1	2050	1200	30,000	33.0	11.3	9.6	0.07375
40B-2	2050	1200	25,000	104.5	6.4	7.2	
40B-3	2050	1200	17,000	1490.5	1.2	5.2	0.0079
41A-1	2050	1200	30,000	215.7	17.5	12.9	0.0172
41A-2	2050	1200	25,000	656.6	21.6	17.3	0.0055
41A-4	2020	1350	15,000	258.3	20.2	19.4	0.0320
41A-5	2050	1350	12,000	1017.6	15.2	8.0	0.0066
41A-6	2050	1350	20,000	44.0	23.3	15.6	0.2250
41A-7	1950	1200	25,000	677.1	15.7	9.3	0.0055
41A-8	1950	1200	- - -				
41A-9	1750	1200	25,000	234.2	26.4	21.9	0.0500
41A-10	1750	1200	20,000	763.1	22.6	12.2	0.0132
41A-11	1850	1200	25,000	926.8	16.2	15.2	
41B-1	2050	1200	30,000	370.7	8.5	5.3	
41B-2	2050	1200	35,000	126.5	12.6	6.1	
41B-3	2050	1200	25,000	1000.2	3.5	- - -	
42A-1	2050	1200	25,000	530.2	19.6	9.7	0.00928
42A-2	2050	1200	30,000	174.8	21.6	17.3	0.03780
42A-3	2050	1200	20,000	2760.8	16.0	10.0	0.00207
42B-1	2050	1200	25,000	945.0	12.8	2.2	
42B-2	2050	1200	30,000	216.2	15.8	6.6	
42B-3	2050	1200	22,500	1743.9	13.4	11.8	
43A-1	2050	1200	25,000	810.4	19.5	10.4	0.00758
43A-2	2050	1200	30,000	228.0	24.9	13.3	0.0330
43A-3	2050	1200	20,000	2884.9	14.2	7.8	0.00177
43A-4	1950	1200	- - -				
43A-5	1950	1200	25,000	766.0	21.5	18.3	0.00998
43A-6	1750	1200	25,000	640.0	32.6	28.1	0.01800
43A-7	1750	1200	30,000	206.7	36.3	22.7	0.05500

TABLE III continued

Specimen No.	Heat Treatment °F	Test Temp. °F	Stress psi	Rupture Life hours	R.A. %	Elong. %	Min. Creep Rate %/hr.
43B-1	2050	1200	30,000	367.7	26.1	15.5	
43B-2	2050	1200	35,000	81.7	27.9	24.4	
43B-3	2050	1200	25,000	1137.3	24.4	14.0	
44A-1	2050	1200	25,000	147.0	30.2	18.5	0.02640
44A-2	2050	1200	20,000	819.9	32.0	26.7	0.00350
44A-3	2050	1200					
44B-1	2050	1200	30,000	128.0	33.9	22.4	0.09500
44B-2	2050	1200	25,000	517.3	28.7	27.2	0.01914
44B-3	2050	1200	20,000	1203.1	25.0	19.2	0.00759
44C-1	2050	1200	30,000	182.0	32.6	18.1	
44C-2	2050	1200	25,000	755.7	26.5	22.0	
44C-3	2050	1200	---				
57A-1	2050	1200	20,000	135.5	30.9	28.5	0.1380
57A-2	2050	1200	15,000	874.1	22.0	17.5	0.0110
57A-3	1750	1200	15,000	746.4	48.8	30.0	
57A-4	1750	1200	---				
57B-1	2050	1200	35,000	4.3	43.8	34.2	
57B-2	2050	1200	20,000	669.7	54.3	46.4	
58A-1	2050	1200	30,000	76.0	27.8	18.9	0.1580
58A-2	2050	1200	20,000	1396.7	21.1	17.8	0.00583
58B-1	2050	1200	30,000	151.0	19.7	16.8	0.03650
58B-2	2050	1200	25,000	370.4	12.5	11.1	0.01002
60A-1	2050	1200	20,000	310.8	19.7	16.7	
60A-2	2050	1200	17,000	815.3	15.4	11.1	
60B-1	2050	1200	30,000	166.3	18.6	15.5	
60B-2	2050	1200	25,000	762.3	13.1	14.1	
61A-1	2050	1200	25,000	48.3	28.2	27.4	0.3200
61A-2	2050	1200	17,000	856.2	18.0	17.8	0.0099
61B-1	2050	1200	30,000	161.4	54.0	39.4	0.1620
61B-2	2050	1200	25,000	603.0	43.9	31.0	0.0258

TABLE III concluded

Specimen No.	Heat Treatment °F	Test Temp. °F	Stress psi	Rupture Life hours	R. A. %	Elong. %	Min. Creep Rate %/hr.
62A-1	2050	1200	25,000	661.1	11.0	12.5	0.00480
62A-2	2050	1200	30,000	163.4	17.2	15.0	
62B-1	2050	1200	35,000	194.3	11.6	9.8	
63A-1	2050	1200	20,000	60.3	52.2	50.4	
63A-2	2050	1200	15,000	291.3	44.8	41.6	
63B-1	2050	1200	25,000	687.3	23.4	18.5	0.01260
63B-2	2050	1200	30,000	131.9$\pm$8	26.1	22.2	0.08220
64A-1	2050	1200	20,000	76.8	52.0	48.9	
64A-2	2050	1200	15,000	770.1	46.0	44.9	
64B-1	2050	1200	30,000	109.6	48.8	46.8	
65A-1	2050	1200	30,000	199.3	12.4	12.0	
65A-2	2050	1200	25,000	796.8	10.3	11.3	
65B-1	2050	1200	30,000	312.9	22.8	12.0	0.01465
65B-2	2050	1200	35,000	89.7	24.4	16.3	0.0765
66A-1	2050	1200	25,000	18.0$\pm$	73.5	69.5	
66A-2	2050	1200	16,000	648.2	63.0	55.7	
66B-1	2050	1200	25,000	1759.9	32.2	26.2	
66B-2	2050	1200	30,000	517.4	33.2	25.4	
10A-7	1950	1200	20,000	57.5	70.0	91.0	0.5380
10A-8	1950	1200	15,000	377.5	62.0	85.0	0.1000
10A-9	1950	1200	12,000	1240.1	56.0	63.0	0.0211
10A-10	1750	1200	18,000	82.2	80.0	84.0	0.4200
10A-11	1750	1200	14,000	490.6	69.0	76.0	0.05630
10A-12	1750	1200	11,500	1074.0	73.0	98.0	0.02880

TABLE IV

1000-Hour Rupture Properties of the Laboratory Heats

Heat No.	Primary Composition Variable %C	%N	Other, %		Temp. of Heat Treatment °F	Test Temp. °F	1000 hr. Rupture Strength ksi	Rupture Curve Slope at 1000 hours	Estimated Ductility on Rupture in 1000 hours R.A..%	Elong..%
1310A	0.009	0.01	--	--	1950	1200	12.5	.175	57	65
					1750	1200	11.8	.175	73	98
1357A	0.05	--	--	--	2050	1200	14.7	.155	22	17
					1750	1200	14.2		50	32
1362A	0.07	0.09	--	--	2050	1200	23.5	.130	10	11
1341A	0.06	0.087	--	--	2050	1350	12.0	.155		
					2050	1200	23.5	.155	25	19
					1950	1200	23.5	-	17	11
					1850	1200	24.5	-	16	15
					1750	1200	19.0	.190	21	10
1341B	0.13	0.090	--	--	2050	1200	25.2		5	4
1342A	0.03	0.10	--	--	2050	1200	22.5	.146	18	10
1342B	0.07	0.11	--	--	2050	1200	25.0	.130	13	9
1361A	0.03	0.05	--	--	2050	1200	16.8	.130	18	17
1343A	0.02	0.145	--	--	2050	1200	24.0	.160	19	10
					1950	1200	24.0	-	21	18
					1750	1200	23.2	.160	31	28
1343B	0.02	0.2	--	--	2050	1200	25.5	.160	24	14
1340A	0.01	0.12	.08 Mn		2050	1200	17.0	.150	5	5
1340B	0.04	0.13	.08 Mn		2050	1200	18.0	.150	5	4
1363A	0.02	--		15ppm B	2050	1200	12.0	.160	35	30
1363B	0.02	0.12		15ppm B	2050	1200	24.0	.110	22	17
1366A	0.06	--	-	15ppm B	2050	1200	15.0	.130	60	54
1366B	0.06	0.12	-	15ppm B	2050	1200	27.5	.150	25	20
1364A	0.02	--	.03 Ti	-	2050	1200	14.5	.123	45	44
1364B	0.02	0.12	.03 Ti	-	2050	1200	22.0	-	(35)	(33)
1344A	0.06	--	.035 Ti	-	2050	1200	19.5	.130	32	27
1344B	0.06	0.12	.035 Ti	-	2050	1200	23.0	{ .128 .240	21	20
1344C	0.06	0.14	.08 Ti	-	2050	1200	24.0	.130	26	22
1338A	<0.02	--	.03 Ti	15ppm B	2050	1200	15.0	.122	56	43
1357B	0.05	--	.03 Ti	15ppm B	2050	1200	18.5	-	56	48
1337A	0.06	--	.03 Ti	15ppm B	2050	1200	26.5	.122	20	10
1361B	0.03	0.07	.03Ti	15ppm B	2050	1200	23.2	.130	42	30
1338B	<0.02	0.13	.03 Ti	15ppm B	2050	1200	27.5	{ .104 .245	32	20
					1750	1200	22.5	.140	45	36
1339A	0.07	0.124	.03	15ppm B	2050	1350	11.5		37	22
					2300	1200	29.0	.230	(25)	(15)
					2050	1200	29.0	.110 and (.245)	23	15
					1950	1200	27.5	-	(26)	(19)
					1850	1200	24.4	-	(24)	(16)
					1750	1200	19.5	.160	45	35
1339B	0.07	0.13	.03 Ti	30ppm B	2050	1200	27.5		20	12
1362B	0.16	0.13	.025 Ti	15ppm B	2050	1200	28.0	-	8	6
1358A	<0.02	0.12	.03 Al	-	2050	1200	21.0	.090	21	18
1358B	0.05	0.13	.03 Al	-	2050	1200	20.2	.210	10	10
1360A	0.08	--	.03 Al	-	2050	1200	16.6	.150	15	11
1360B	0.08	0.12	.03 Al	15ppm B	2050	1200	24.3	.110	13	13
1365A	0.06	0.12	.19 Cu	-	2050	1200	24.2	.130	10	11
1365B	0.06	0.13	.19 Cu	.20 Mo	2050	1200	25.6	.120	21	11

TABLE V

The Influence of Trace Amounts of Titanium and Boron
in Type 304 Laboratory Heats of Varying Carbon and
Nitrogen Content

Key: (a) 1000 hour rupture strength, ksi.
(b) Estimated elongation for rupture in 1000 hours, percent
(c) Heat number

%C	%N	B (ppm) → Ti (%) →	None None	15 None	None .02-.04	15 .02-.04
.01-.02	<.01	(a)	12.5	12.0	14.7	15.0
		(b)	63	30	44	43
		(c)	1310A	1363A	1364A	1338A
.05-.07	<.01	(a)	15.5	15.0	19.5	26.5
		(b)	17	54	27	10
		(c)	1357A	1366A	1344A	1337A
.01	.12-.14	(a)	24.0	24.0	22.0	27.5
		(b)	10	17	(33)	15
		(c)	1343A	1363B	1364B	1338B
.06	.13	(a)	25.0	27.0	21.0	29.0
		(b)	9	20	20	15
		(c)	1342B	1366B	1344B	1339A

TABLE VI

Ferrite Content of Type 304 Steels

Before and After Cold Deformation

Heat Number	Heat Treatment	Ferrite Content as Heat Treated	Ferrite Content as Treated + 50% CW
1310A	2050°F	1.7	28.
	1750	2.3	35.
1310B	2050	0	.8
	1750	.25	-
1338A	2050	3.1	13.0
1338B	2050	0	1.2
1309A	2050	0	4.0
1309B	2050	0	2.3
1318	2050	-	1.3
1344A	2050	0	1.8
1344B	2050	0	0
1337A	2050	.3	0.8
1339A	2050	0	0.65
1339B	2050	0	1.6
1343A	2050	0	.5
1341A	2050	0	.2
1340B	2050	0	1.2
PT9	2050	0	0
	1750	0	.3 at 75% CW
PT8	2050	0	0
	1750	0	0
PT10	1950	0	2.0
PT11	1950	0	2.3
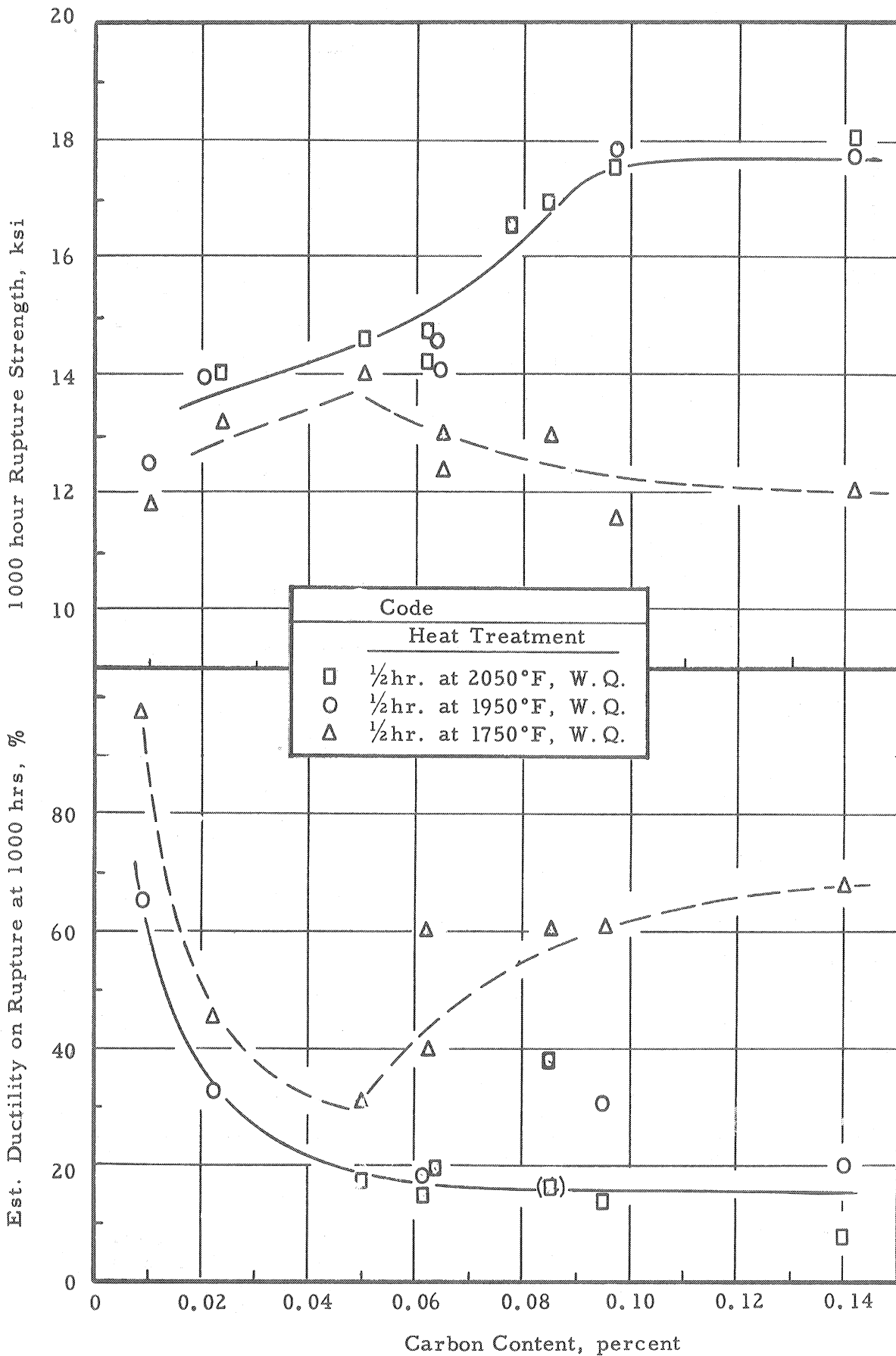
Figure 1. The influence of carbon content and temperature of heat treatment on the 1000-hour rupture strength at 1200°F of laboratory heats of Type 304 steel containing very low nitrogen (<0.01%).
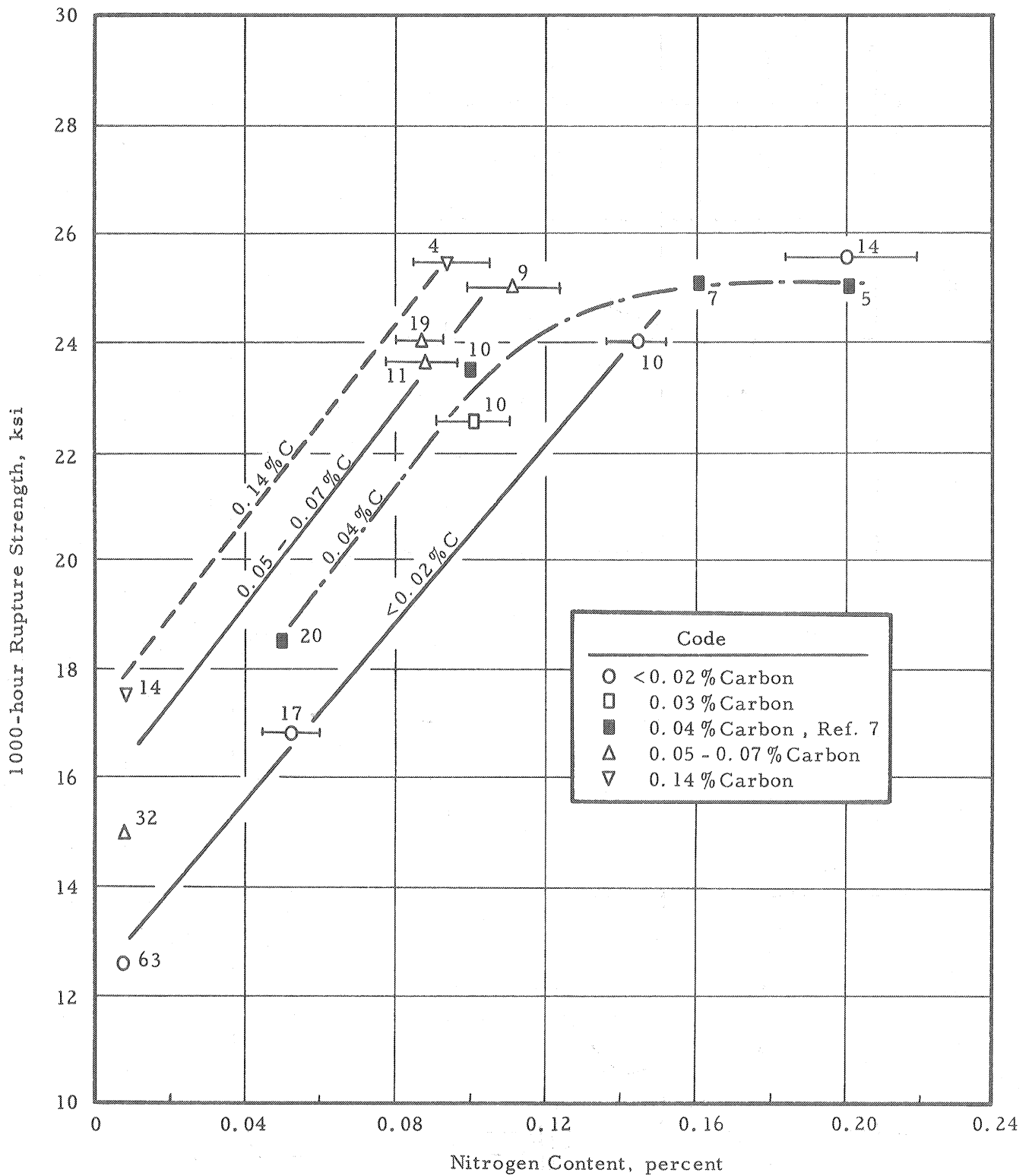
Figure 2. The influence of nitrogen on the 1000-hour rupture strength of Type 304 steel at various carbon levels. The numbers near the symbols are the estimated percent elongation on rupture at 1000 hours.
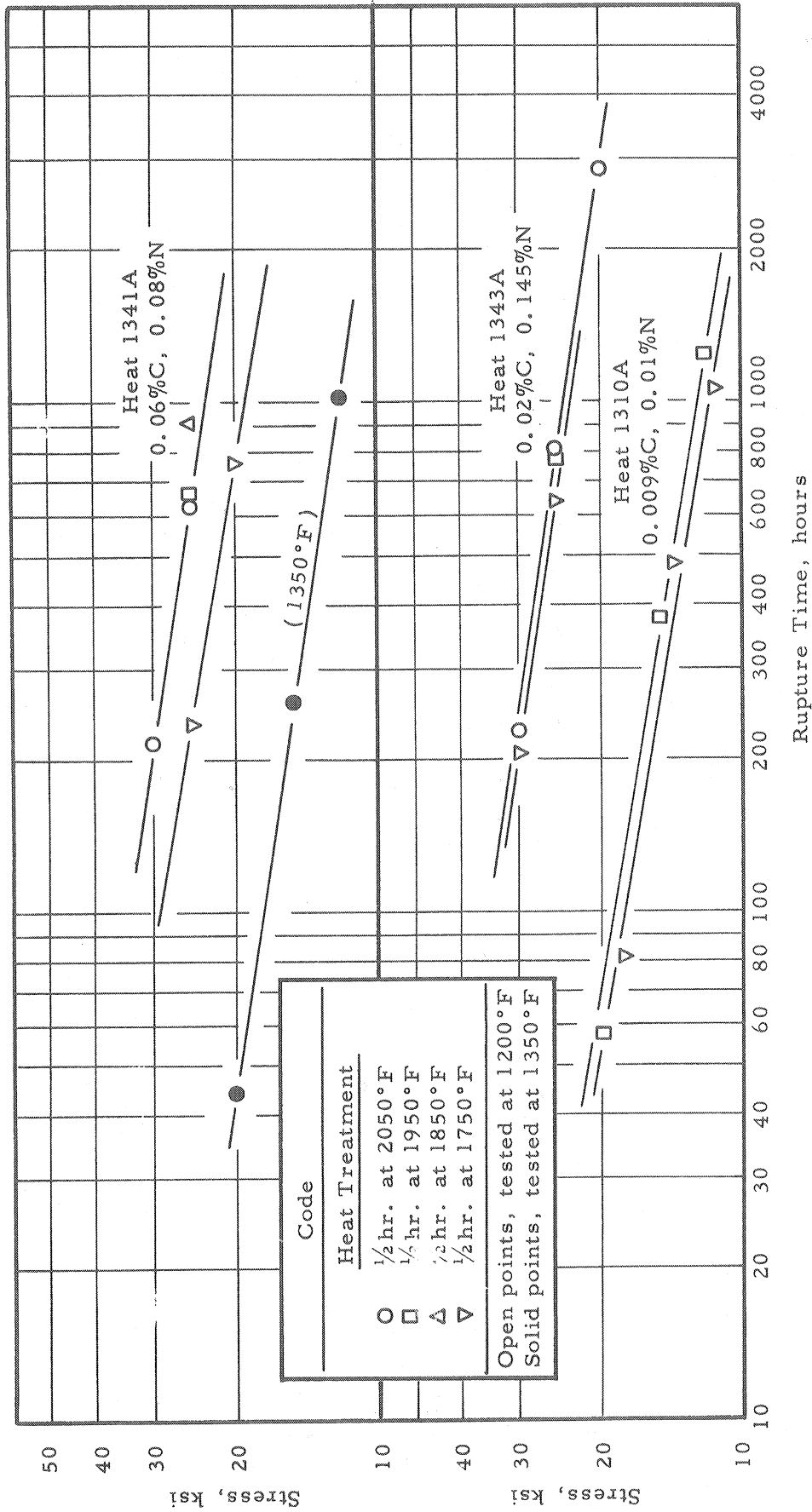
Figure 3. Stress-rupture time curves at 1200° and 1350° F of laboratory heats 1341A, 1343A and 1310A, heat treated as indicated.
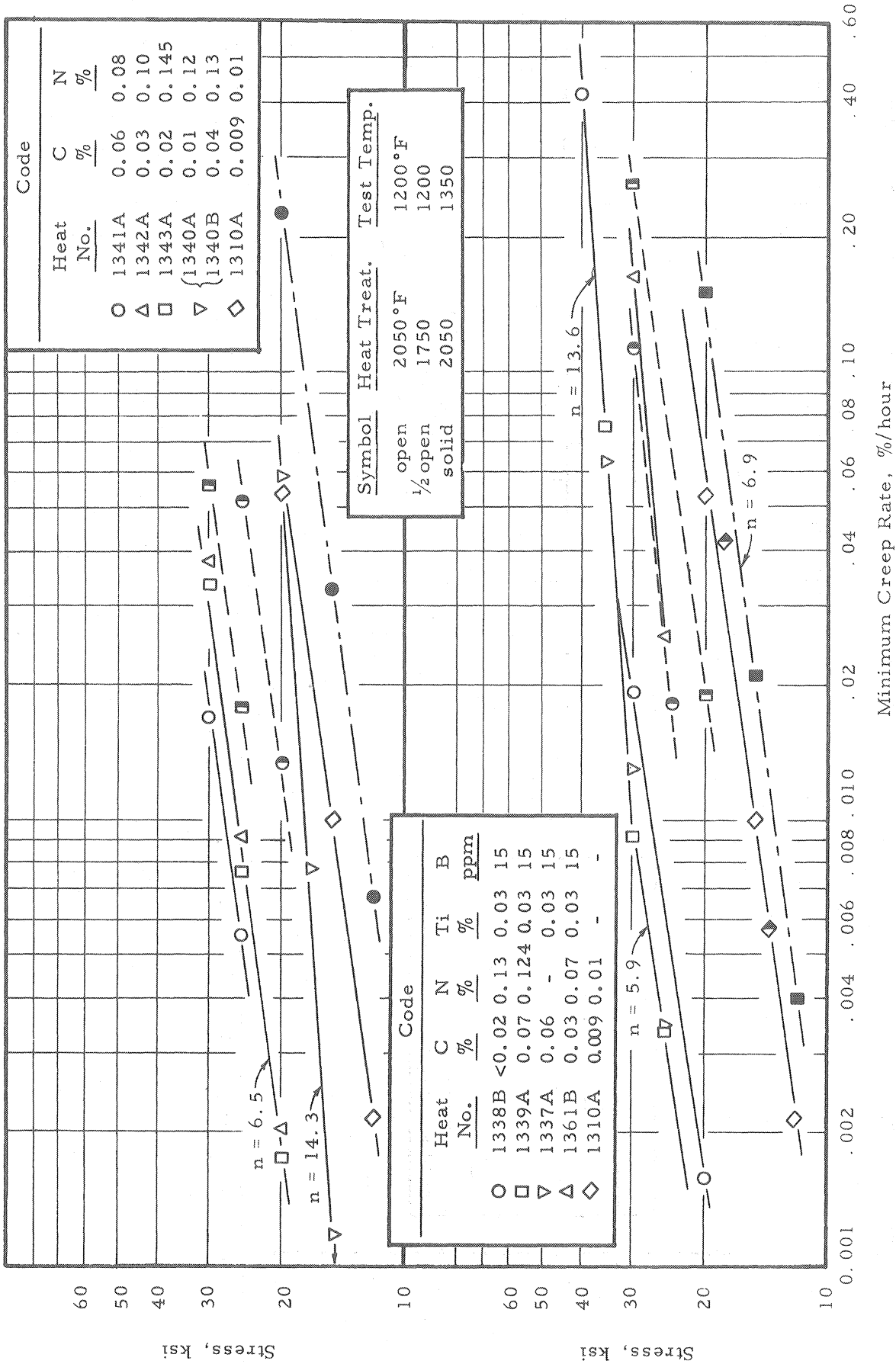
Figure 4. Stress versus minimum creep rate curves for several alloys containing carbon and/or nitrogen, with and without boron and titanium additions. Heat treatments and test temperatures are as indicated. Heat 1310A with very low carbon, nitrogen and residual element content, is shown for reference

Minimum Creep Rate, %/hour

Stress, ksi

Heat No.	C %	N %
1341A	0.06	0.08
1342A	0.03	0.10
1343A	0.02	0.145
{1340A	0.01	0.12
{1340B	0.04	0.13
1310A	0.009	0.01

Code

Symbol	Heat Treat.	Test Temp.
open	2050°F	1200°F
½ open	1750	1200
solid	2050	1350

Heat No.	C %	N %	Ti %	B ppm
1338B	<0.02	0.13	0.03	15
1339A	0.07	0.124	0.03	15
1337A	0.06	-	0.03	15
1361B	0.03	0.07	0.03	15
1310A	0.009	0.01	-	-

Code

n = 13.6
n = 6.9
n = 6.5
n = 14.3
n = 5.9
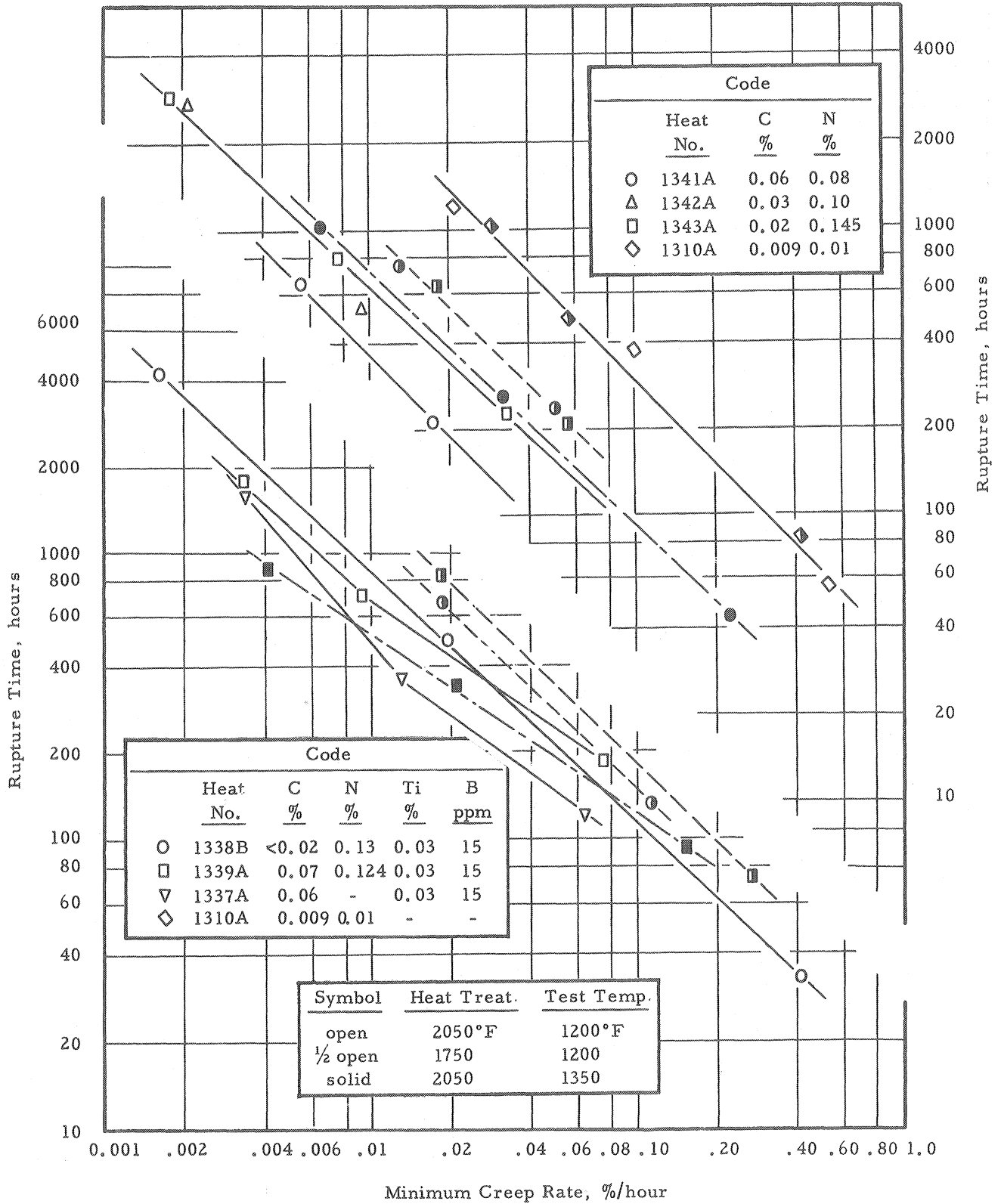
Figure 5. Rupture time versus minimum creep rate for several laboratory heats containing carbon and/or nitrogen, with and without additions of boron and titanium.
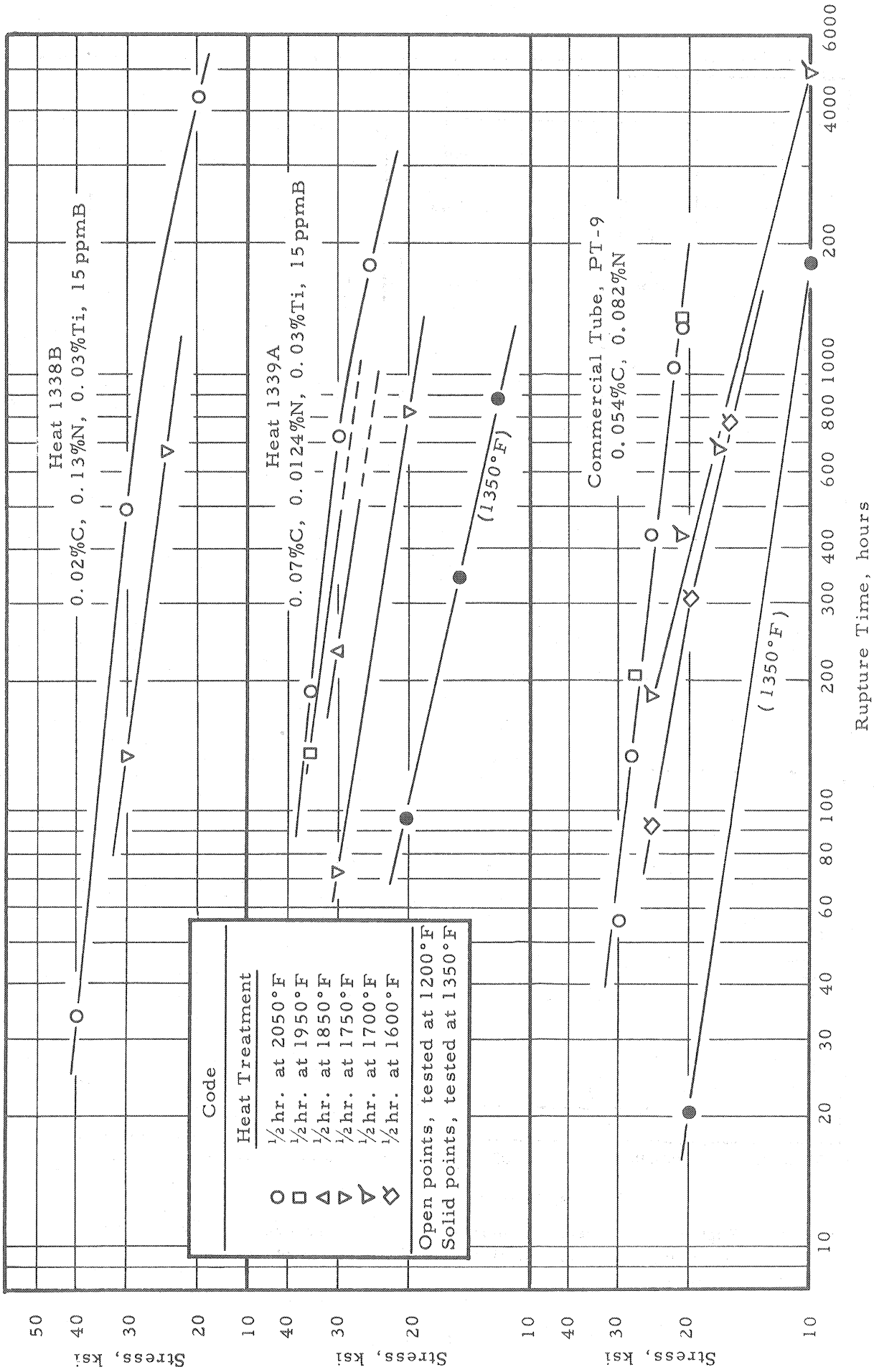
Figure 6 Stress-rupture time curves at 1200°F and 1350°F for laboratory heats 1338B and 1339A and the commercial tube PT-9, heat treated as indicated.

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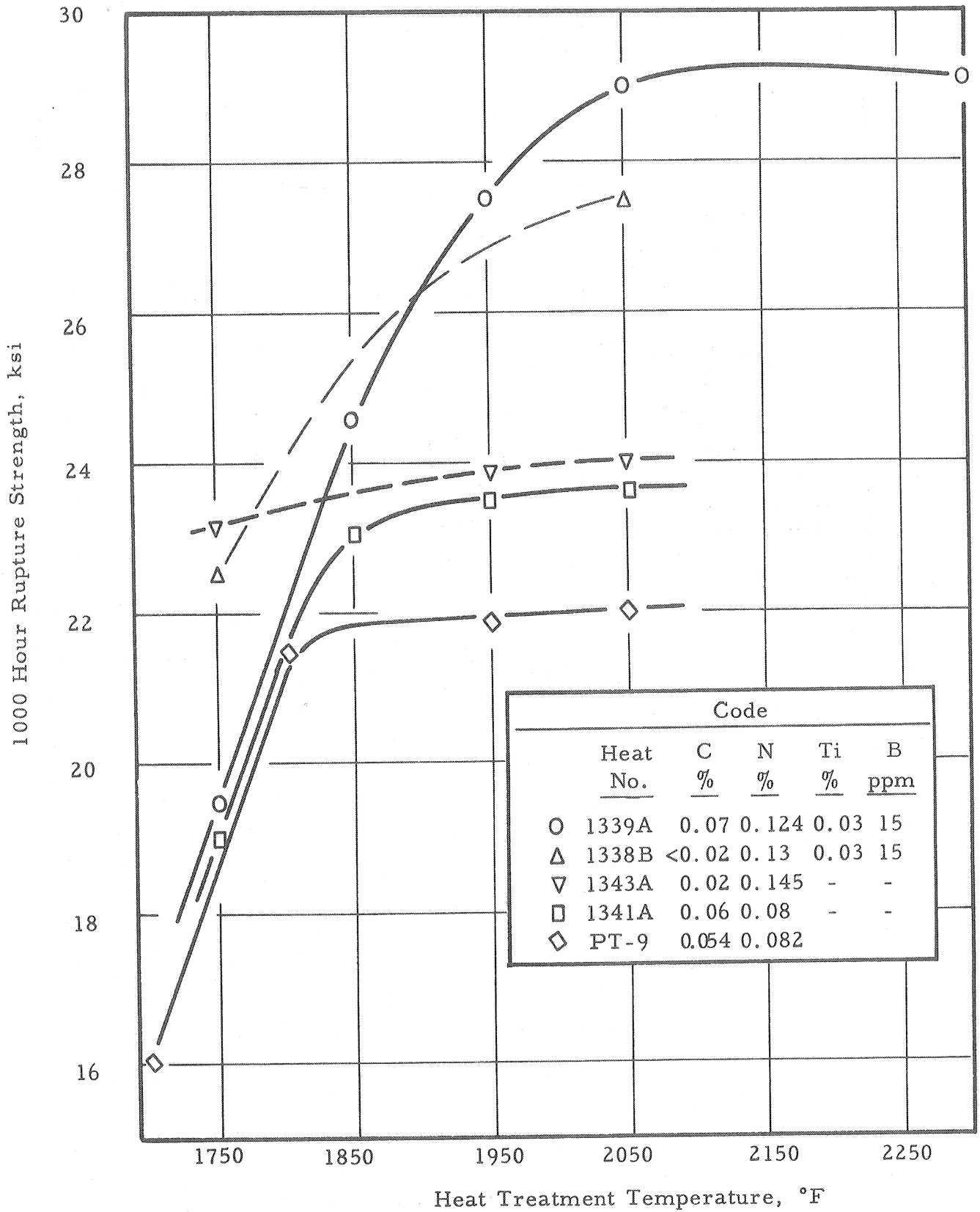
Figure 7. The influence of the temperature of heat treatment on the
1000-hour rupture strength at 1200°F of several laboratory
heats and a commercial tube of Type 304 steel.

65
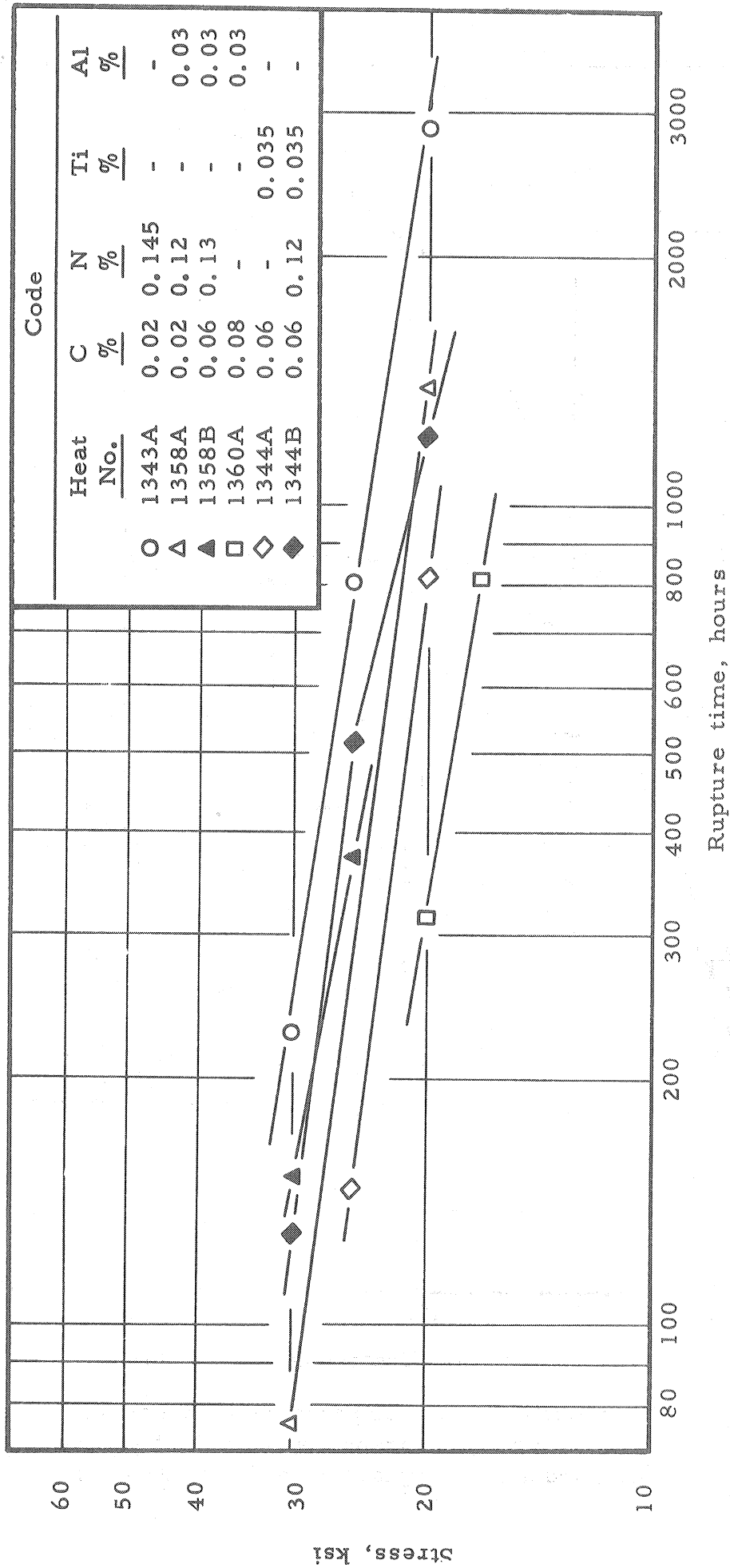
Figure 8. Stress-rupture time curves at 1200°F for laboratory heats with aluminum and titanium additions. Heat 1343A is shown for comparison. All material was heat treated 1/2-hour at 2050°F, W.Q.

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10A-9: 12,000 psi, 1240 hrs.
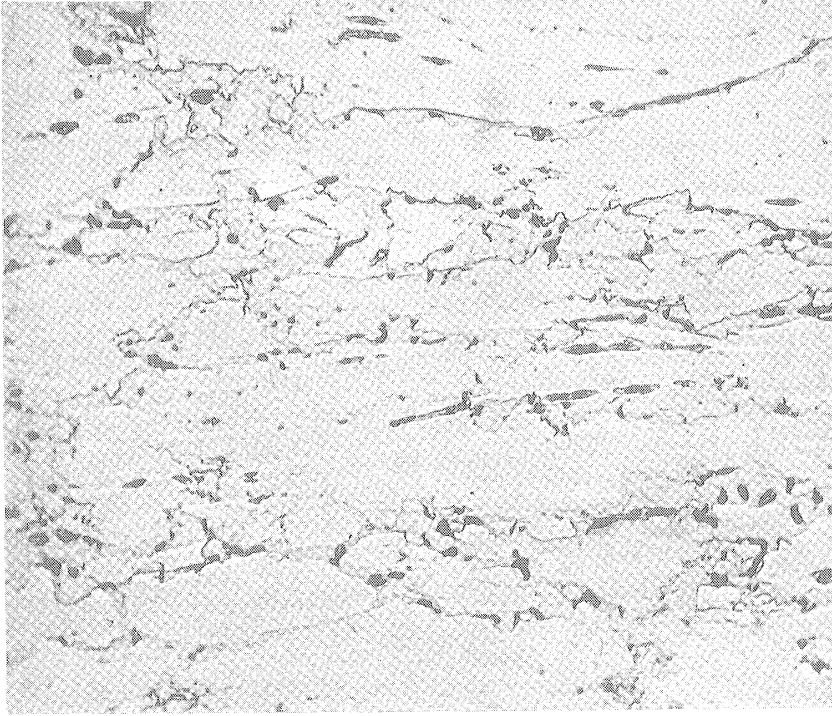
38A-1: 20,000 psi, 111 hrs.
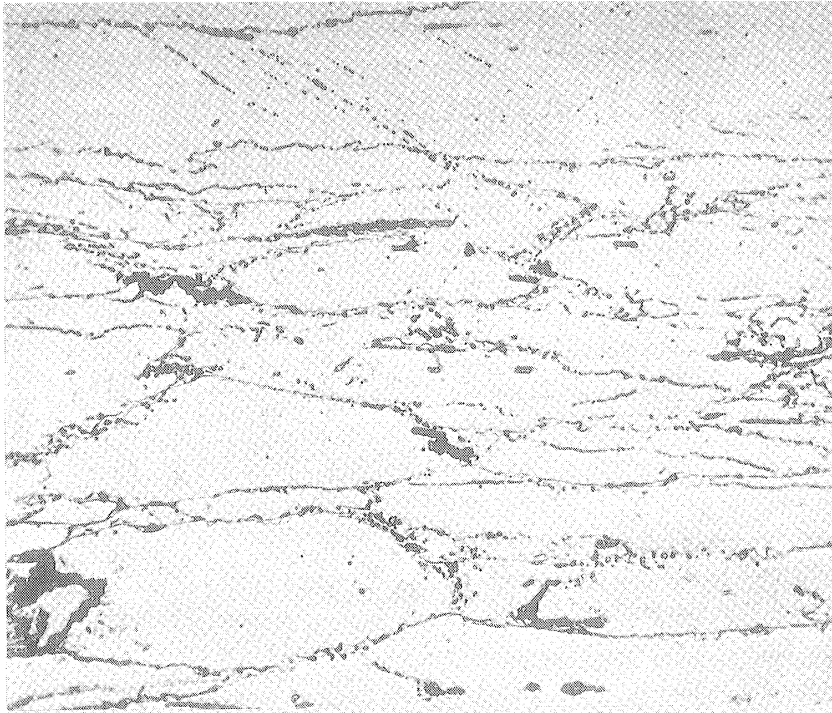
Figure 9. Photomicrographs of specimens from Heats 1310A and 1338A
after rupture testing at 1200°F showing the deformed grains
characteristic of materials with very low carbon and nitrogen
contents. The specimen number, stress, and rupture life are
given above the photomicrographs. Etched electrolytically with
60% HNO_3. Magnification - 500X.

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(a)
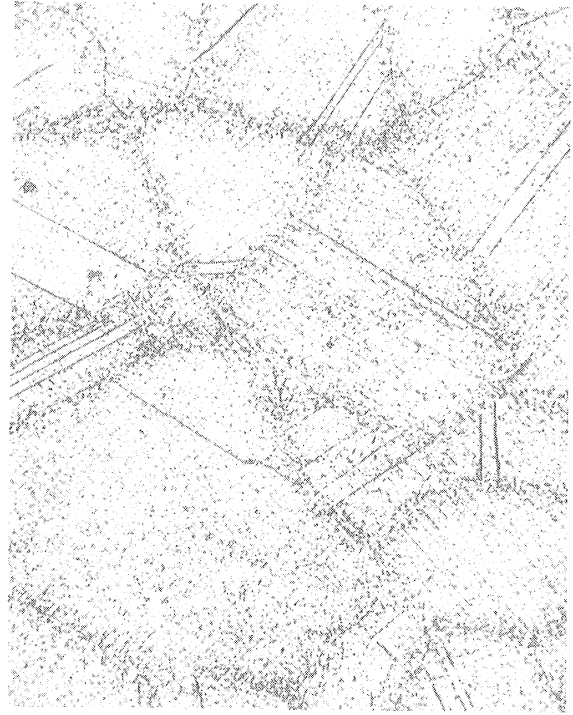
(b)

(c)
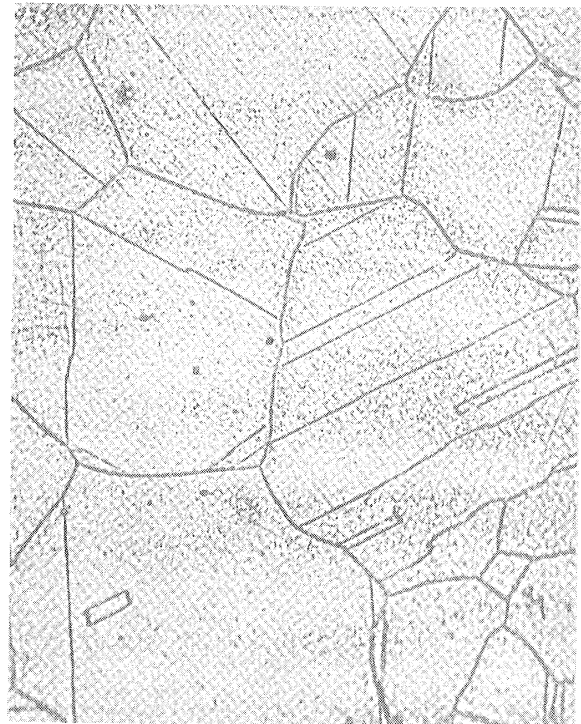
(d)

Figure 10. Photomicrographs of a specimen from Heat 1309 B, heat
treated at 1950°F, tested at 1200°F and 17,000 psi; rupture
time, 1484 hours. Photos (a) and (c) were taken near the
fracture (high stress region); (b) and (d) near the threaded
section of the specimen (low stress region). Etchant: (a)
and (b), 10% chromic acid, electrolytic; (c) and (d), 60%
HNO_3, electrolytic. Magnification - 1000X.

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61A-2: 17,000 psi, 856 hrs.
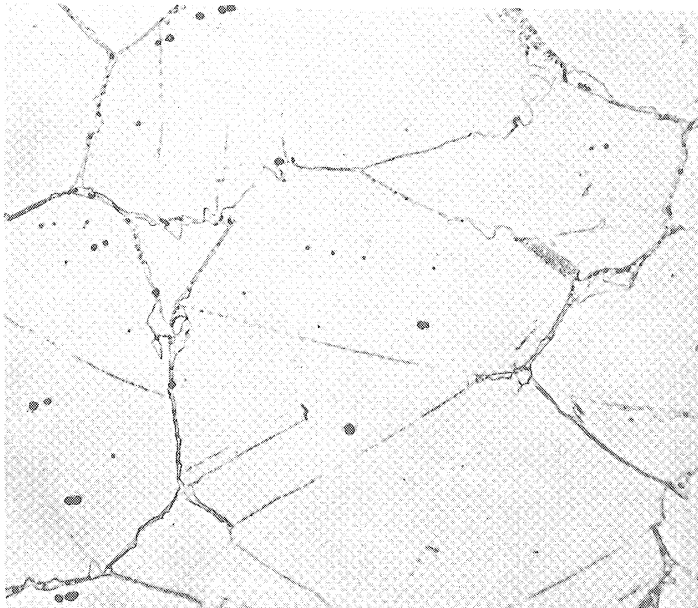
43A-1: 25,000 psi, 810 hrs.
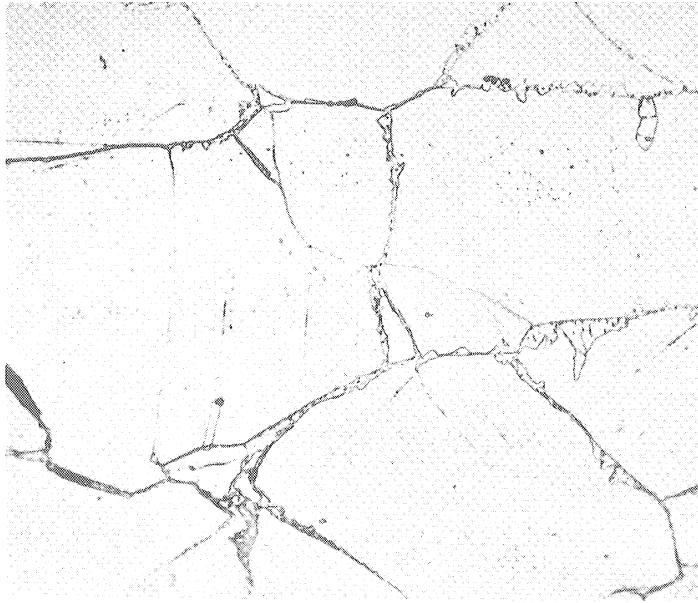
43B-1: 30,000 psi, 368 hrs.

0.06%N

0.145%N
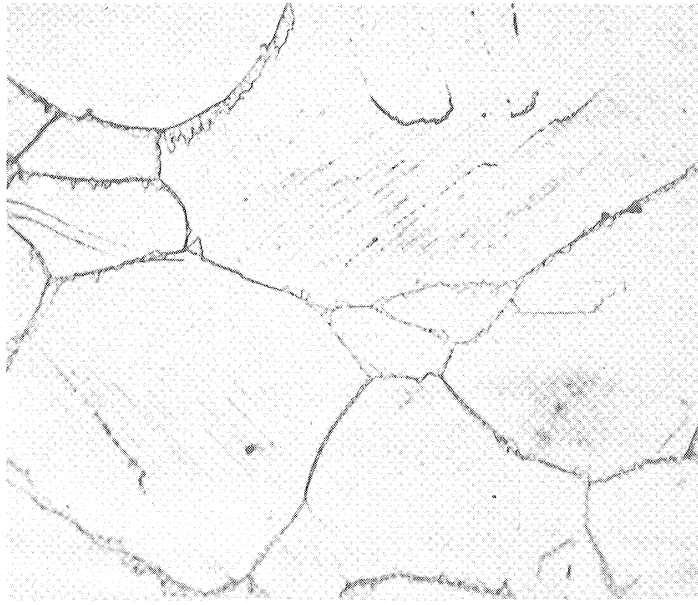
0.23%N

Figure 11. Photomicrographs of specimens from heats of varying nitrogen content with 0.02 percent or less, carbon. Specimens were heat treated at 2050°F prior to testing. The specimen number, stress, and rupture life are given above the photomicrographs. All the specimens are etched electrolytically with 60% HNO₃. Magnification - 500X.
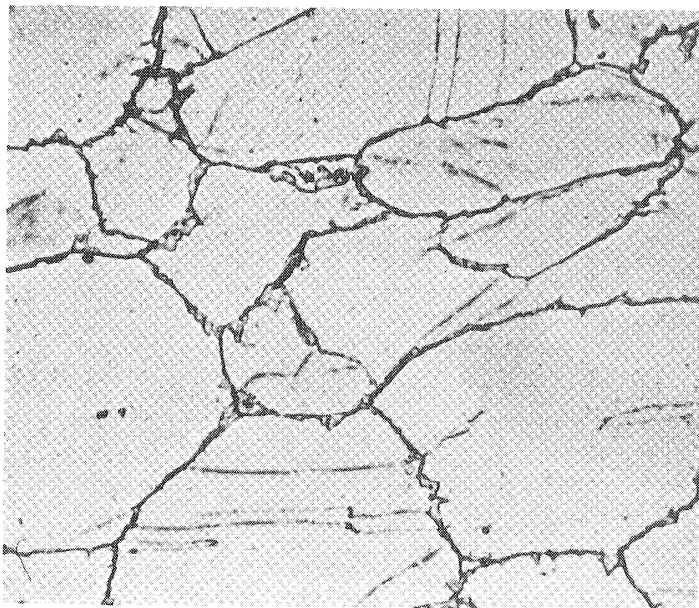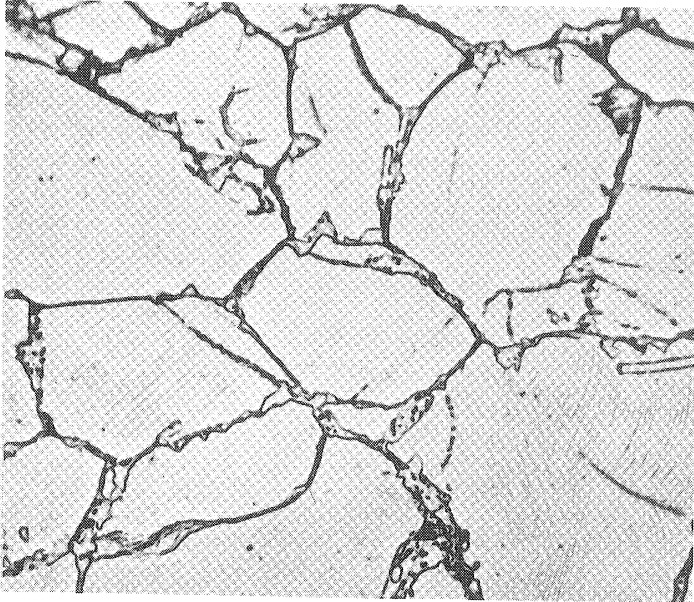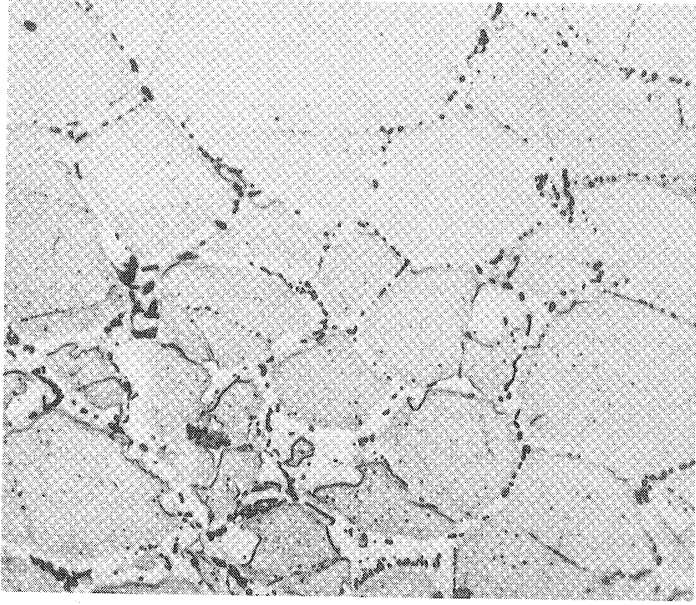
33.7 hours   486 hours   4321 hours

Figure 12. Photomicrographs of specimens from Heat 1338B, tested at 1200°F, showing the "thickening" of the boundaries with increasing time to rupture. The specimens were heat treated at 2050°F prior to testing. Stresses were 40,000, 30,000 and 20,000 psi respectively. Specimens were etched electrolytically with 60% HNO_3. Magnification - 500X.
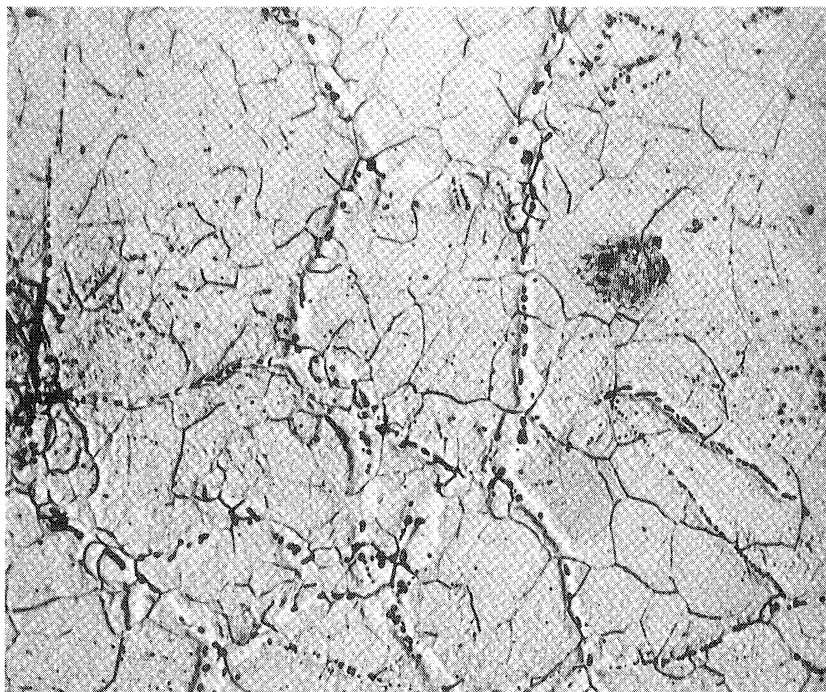
(a)
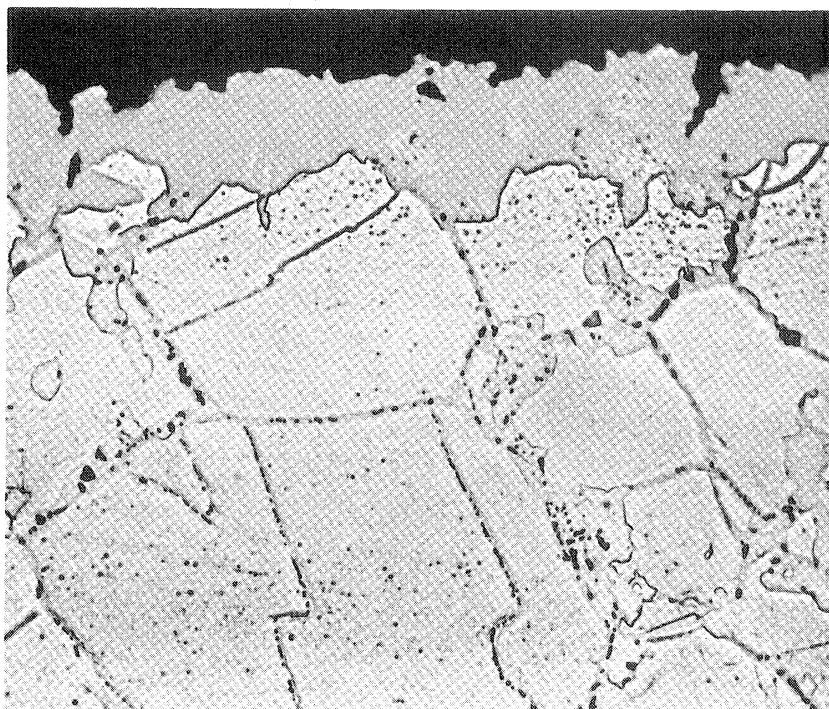
(b)

Figure 13. Photomicrographs of specimen 38B-1 from Heat 1338B.
Heat treated at 2050°F, tested at 1200°F and 20,000 psi.
Rupture time - 4321 hours.
   (a) Recrystallized structure produced by cold working
       and heating for 10 hours at 1400°F, showing "thickening"
       associated with previous grain boundaries.
   (b) Edge of specimen as tested, showing continuity of
       "thickened" boundaries with the depleted surface area.
Etched electrolytically with 60% HNO$_3$.   Magnification - 1000X.

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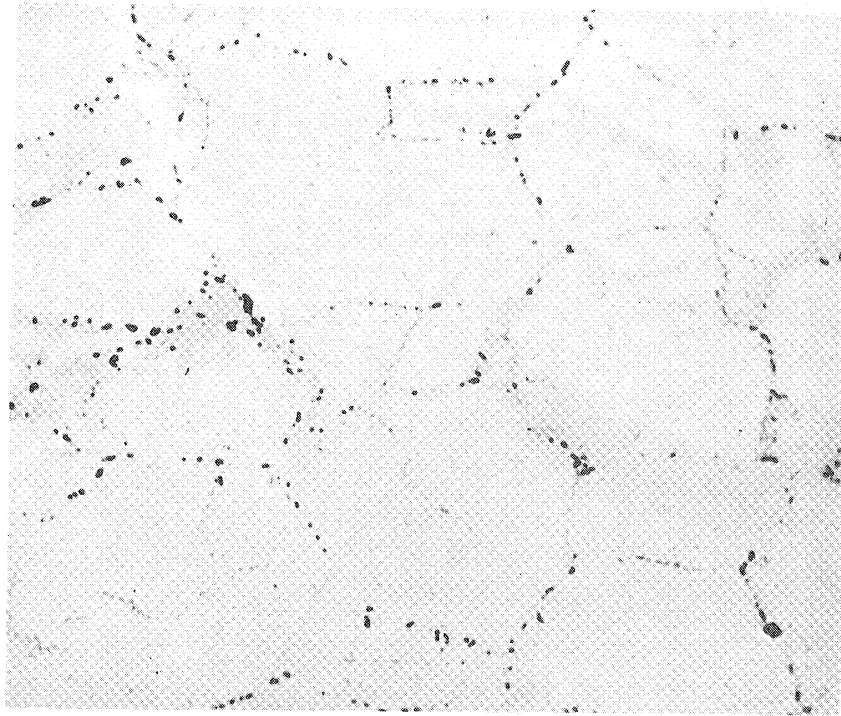
(a) Etched with 10N KOH
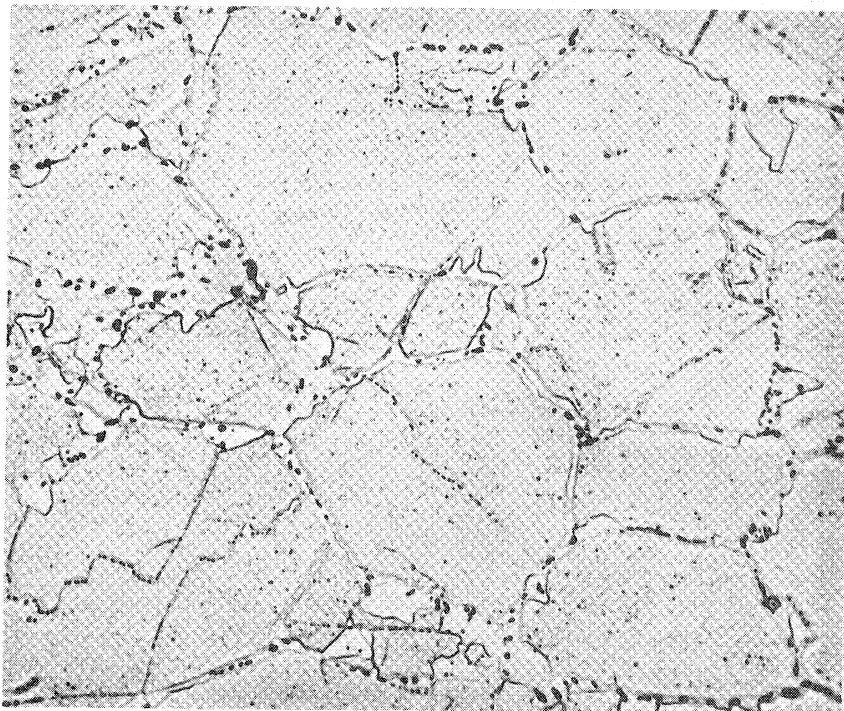
(b) Etched with 60% HNO₃

Figure 14. Photomicrographs of specimen 38B-1 from Heat 1338B.
(a) Etched electrolytically with 10N KOH to reveal
sigma phase.
(b) Etched electrolytically with 60% HNO₃ to bring out
the general structure.
Magnification - 1000X.

Tested at 1200°F
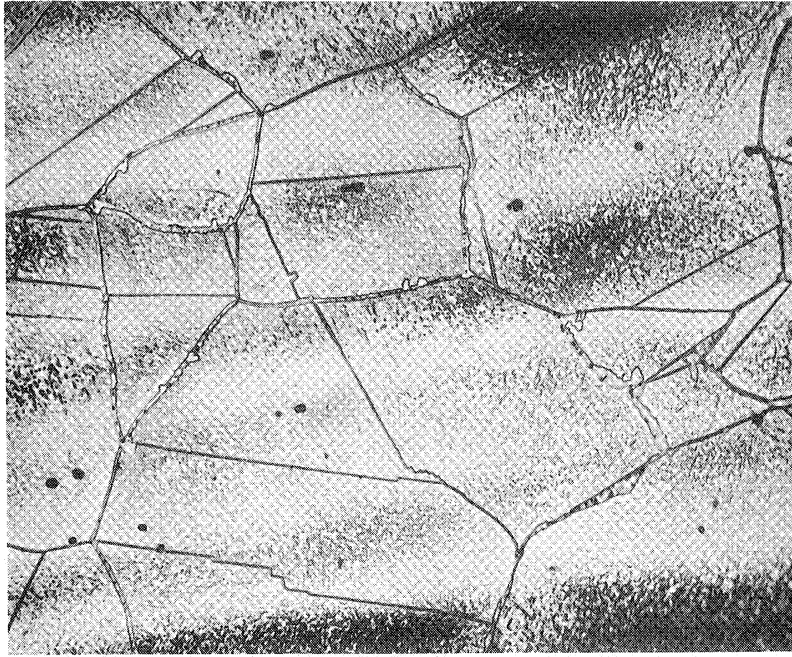
Tested at 1350°F
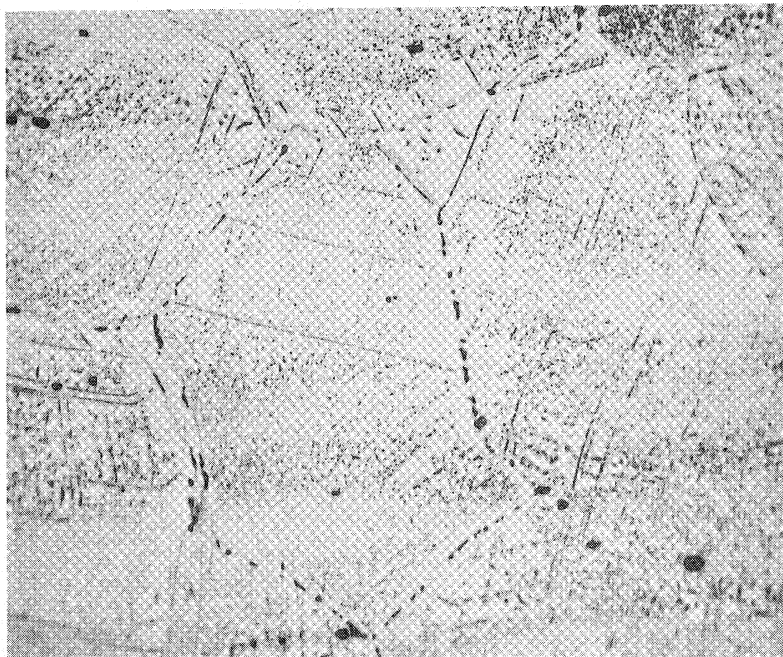
Figure 15. Photomicrographs of specimens from Heat 1341A, heat treated at 2050°F and tested at 1200°F and 25,000 psi and at 1350°F and 12,000 psi. The rupture life of these specimens was 657 and 1018 hours respectively. Etched electrolytically with 60% HNO_3. Magnification - 500X.

57A-2: 15,000 psi, 874 hrs.   44B-2: 25,000 psi, 517 hrs.
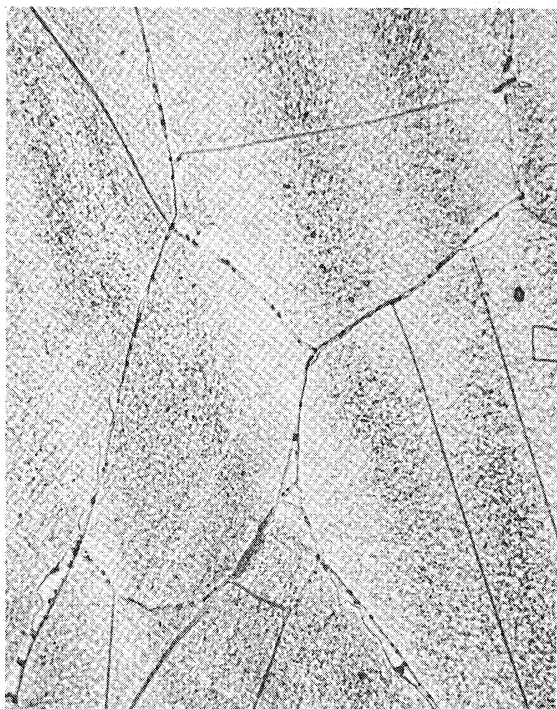
37A-2: 30,000 psi, 370 hrs.   39A-2: 30,000 psi, 721 hrs.
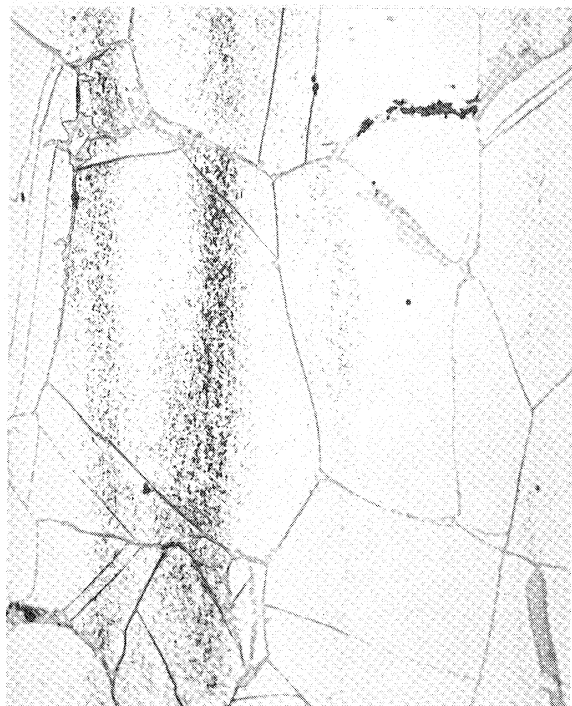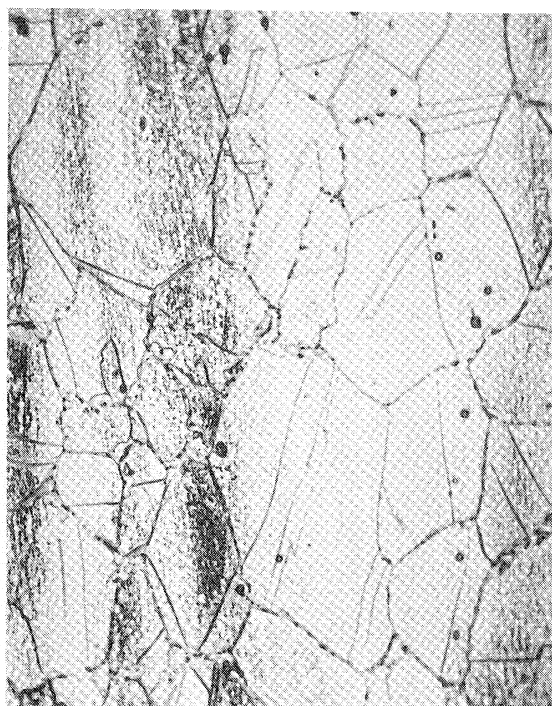
Figure 16. Photomicrographs of specimens from Heats 1357A, 1344B,
1337A, and 1339A, heat treated at 2050°F and tested at
1200°F. The specimen number, stress, and rupture time
are given above each photomicrograph. Etched electrolytically
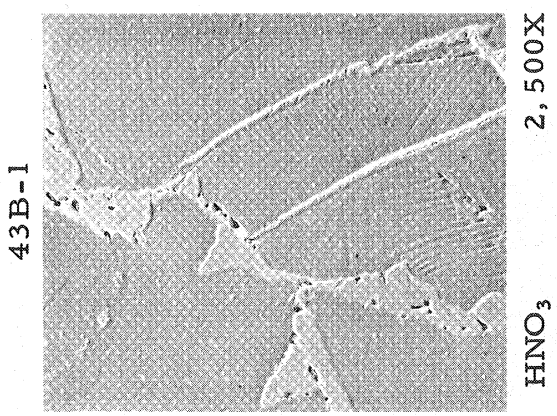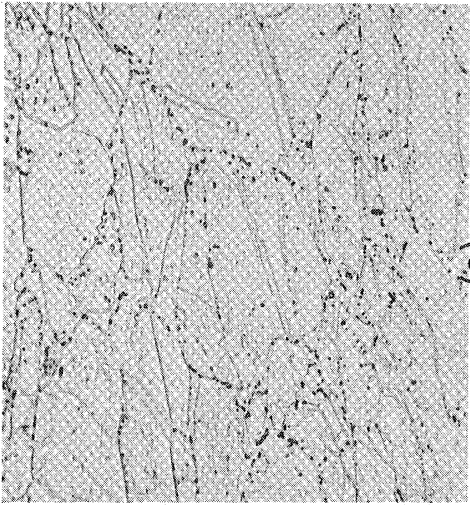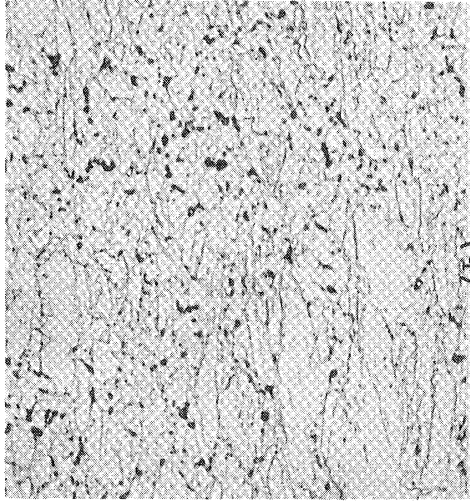with 60% HNO_3. Magnification - 500X.

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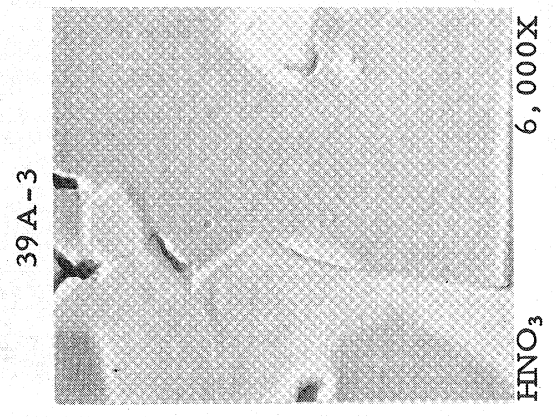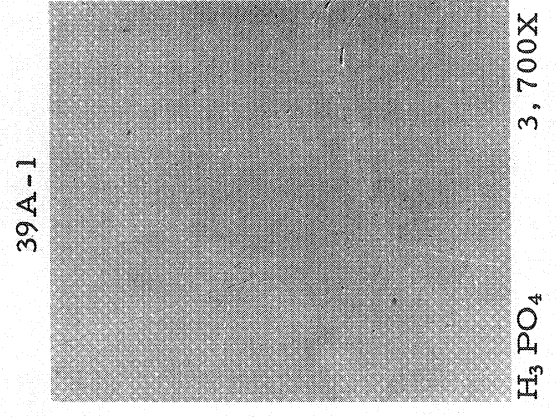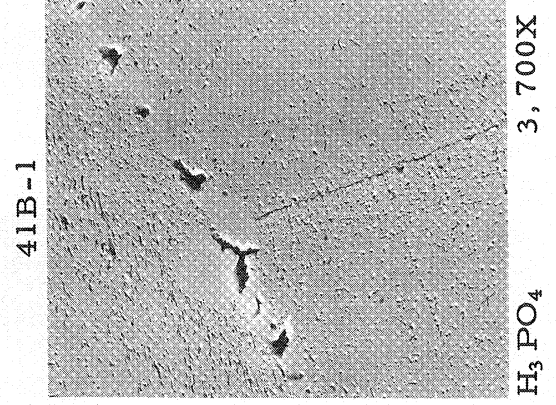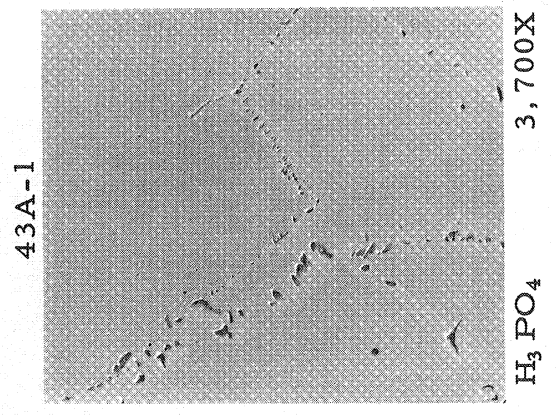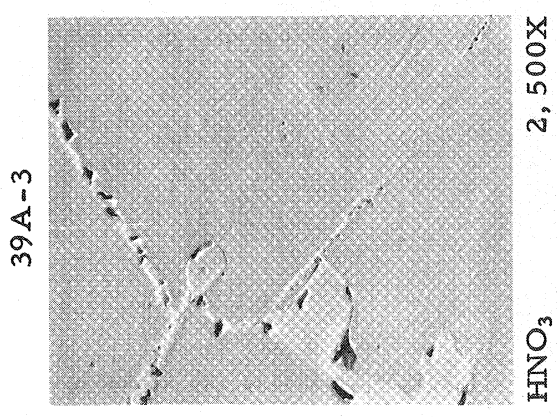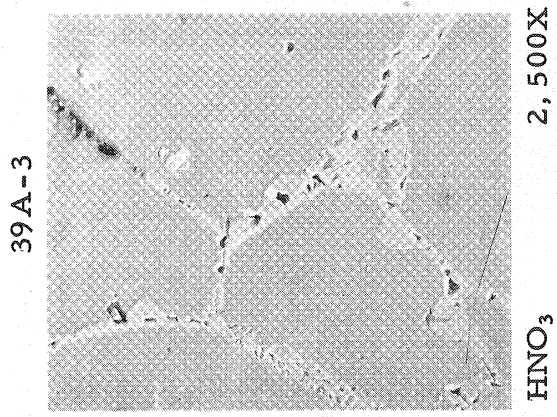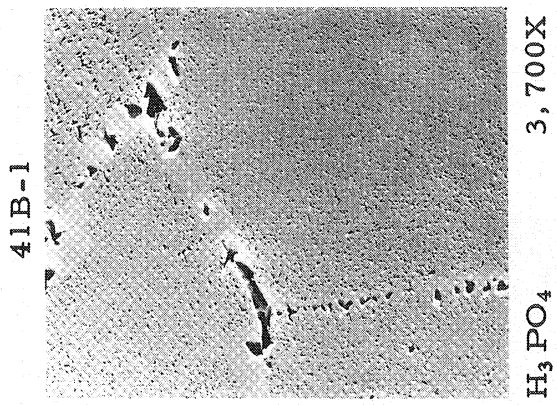
Figure 17. Electron micrographs of several specimens showing various aspects of the microstructure. The figures above the pictures are the specimen code (see Table III), those below are the etchant and the magnification.
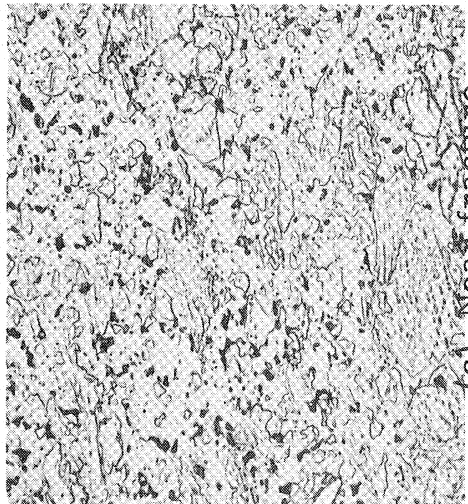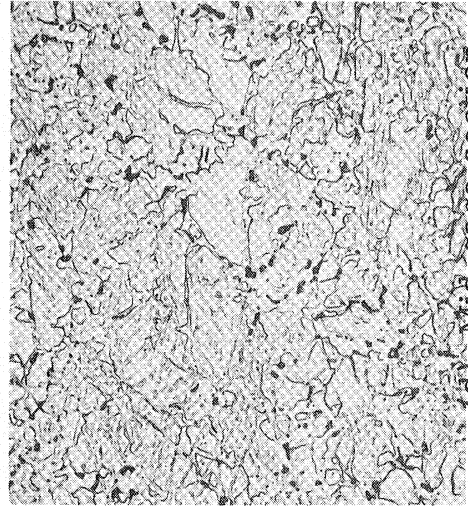
1800°F   1700°F

(a)   (b)

1600°F

1600°F   1600°F

(c) Near fracture   (d) Mid-gage section   (e) Threaded section

Figure 18. Photomicrographs of specimens from commercial tube PT-9, tested at 1200°F. Photomicrographs (a), (b), and (c) were taken near the fractures (i.e., from a high stress region) of specimens heat treated at 1800°, 1700°, and 1600°F respectively. Photomicrographs (c), (d), and (e) of the specimen heat treated at 1600°F before testing, illustrate the microstructural variation between different areas of the specimen. The stress and rupture life of the specimens are as follows: (a), 21,000 psi, 1147 hrs.; (b), 17,000 psi, 682 hrs.; (c), 16,000 psi, 788 hrs. Etched electrolytically with 60% HNO₃. Magnification - 500x.

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57A-3: 15,000 psi, 746 hrs.   43A-6: 25,000 psi, 640 hrs.
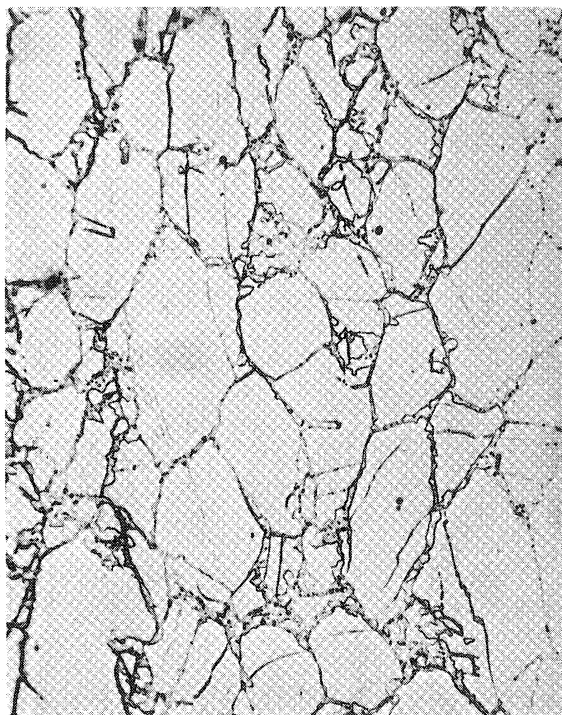
41A-10: 20,000 psi, 763 hrs.   39A-10: 20,000 psi, 825 hrs.
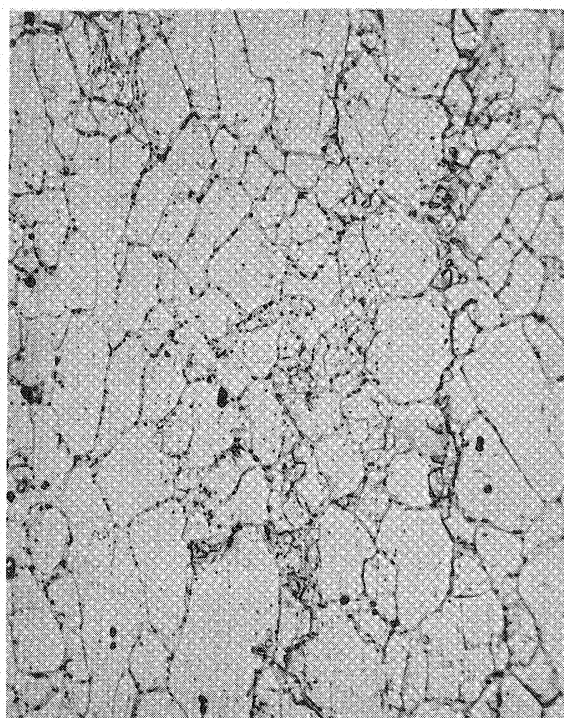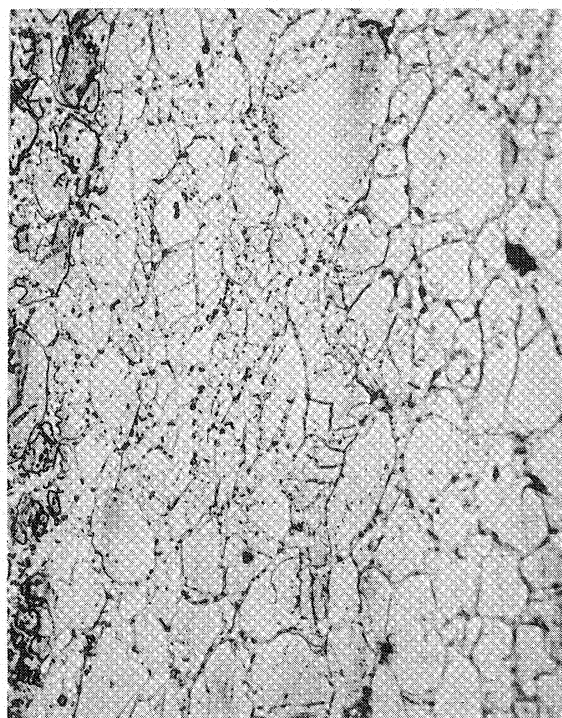
Figure 19. Photomicrographs of specimens from Heats 1357A, 1343A,
            1341A and 1339A heat treated at 1750°F and tested at 1200°F.
            The specimen number, stress and rupture time are given
            above each photomicrograph. Etched electrolytically with
            60% HNO₃. Magnification 500X.

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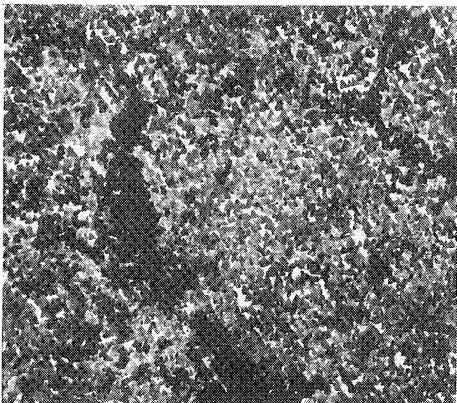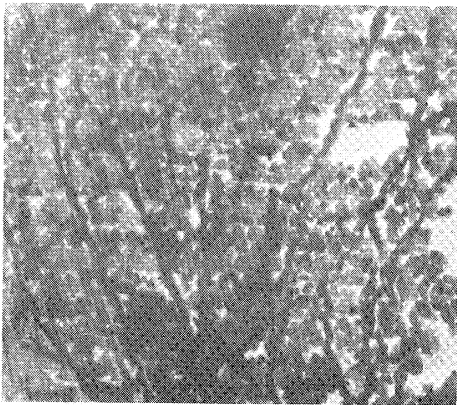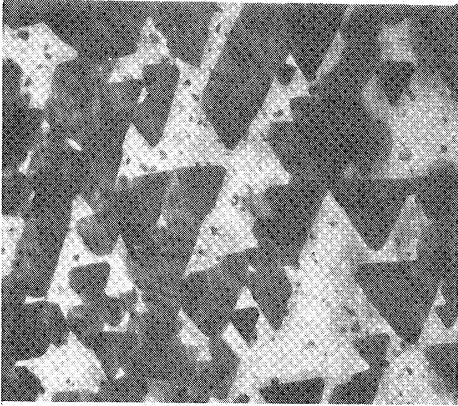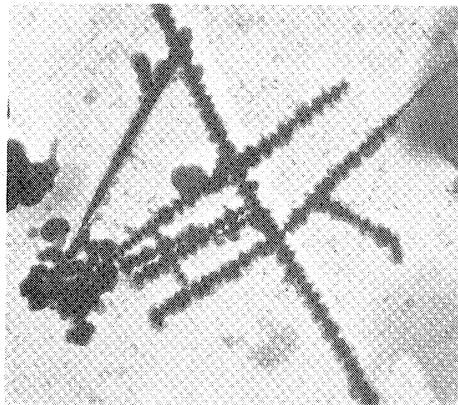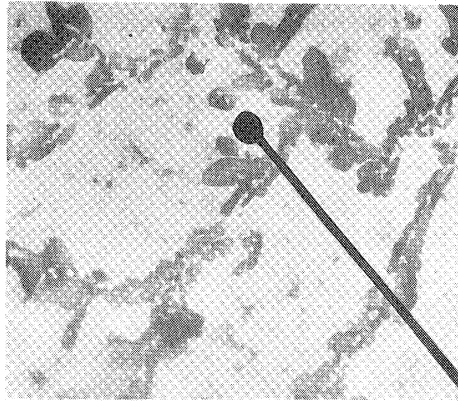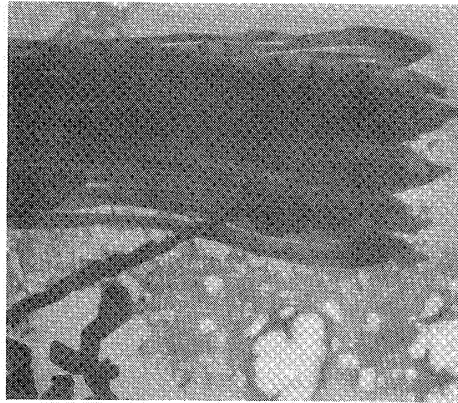
Figure 20. Electron micrographs of particles extracted with HCl-picric mixed acids, from various spe-cimens. The figures above the pictures are the specimen numbers. (See Table III.)

44B-2   (c) 50,000X

39A-3   (b) 12,300X

41A-1   (a) 2,500X

43B-1   (g) 10,000X

43B-1   (f) 5,200X

PT9-2   (e) 15,200X

39A-3   (d) 16,000X

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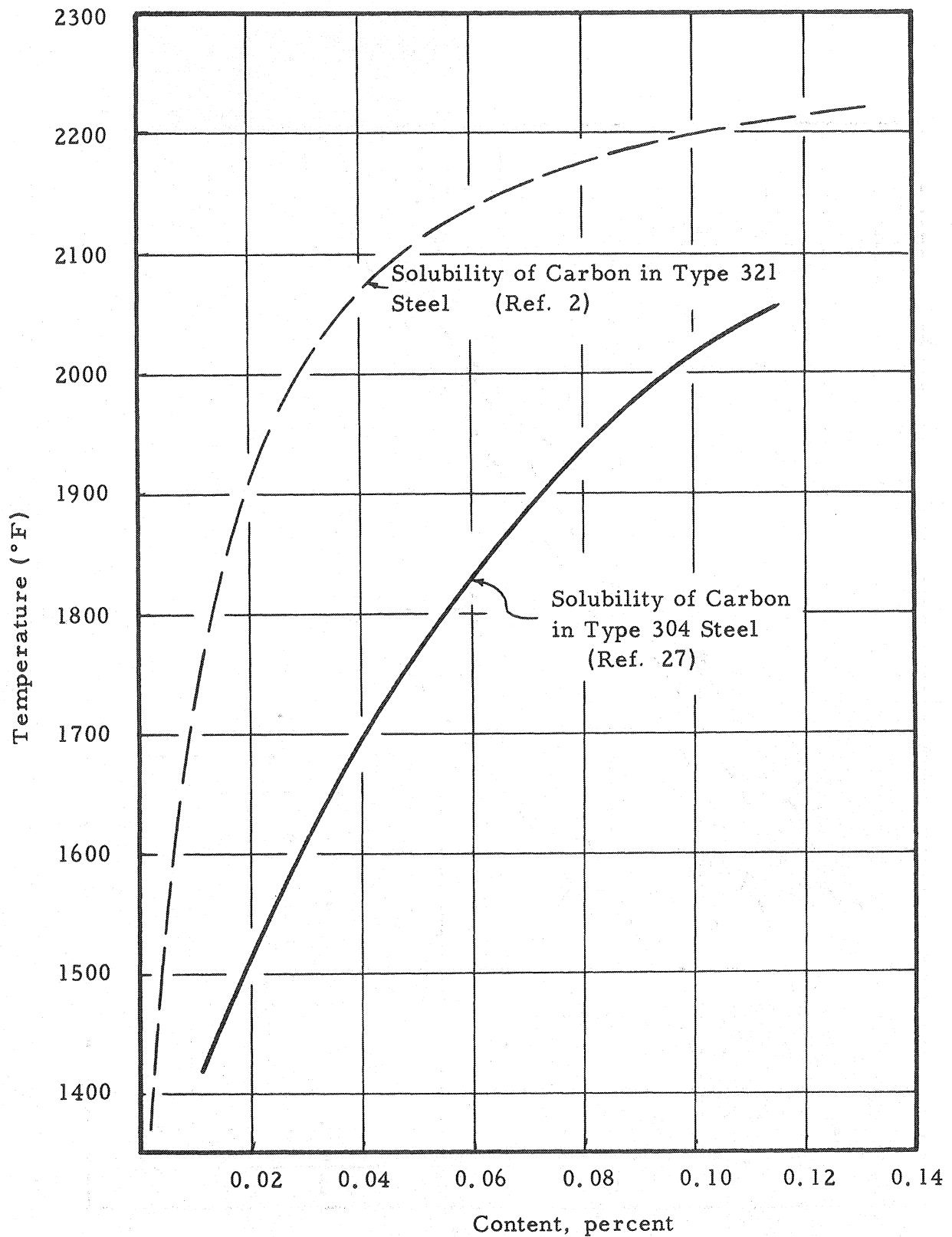
Figure 21. Carbon solubility curve for Type 304, 18%Cr - 10%Ni, austenitic steel — from the data of Rosenberg and Irish[27]. The carbon solubility curve for Type 321 steel, as derived by White and Freeman[2], is shown for comparison.

Time at 1200°F, hrs. ——→

100,000 10,000 1000

1339A
1338B
1337A

1341A}
1343A}

PT-9

1338A
1310A

	Code				
Heat No.	C %	N %	Ti %	B ppm	
1341A	0.06	0.08	-	-	O
1343A	0.02	0.145	-	-	□
PT-9	0.054	0.082	-	-	◇
1339A	0.07	0.124	0.03	15	△
1338B	<0.02	0.13	0.03	15	▽
1337A	0.06	-	0.03	15	◖
1338A	<0.02	-	0.03	15	D
1310A	0.009	0.01	-	-	◊

Open points - Tested at 1200°F
Solid points - Tested at 1350°F

$T (20 + \log t) \times 10^{-3}$

34   35   36   37   38   39   40   41   42   43

Stress, ksi

40   35   30   25   20   15   10   9   8   7   6   5
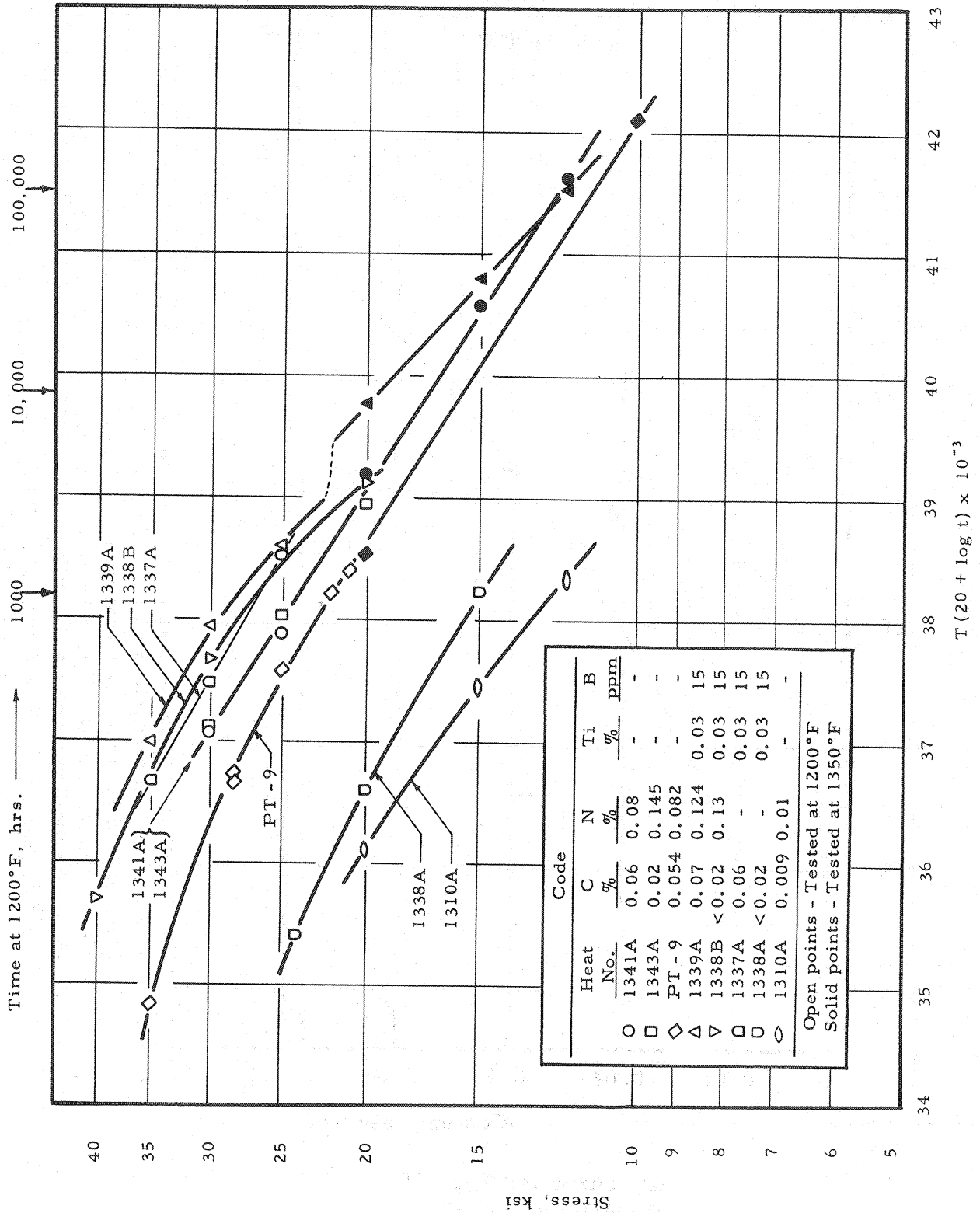
Figure 22. Miller-Larson parameter representation of the stress-rupture time curves of several laboratory heats and of the commercial tube, PT-9.
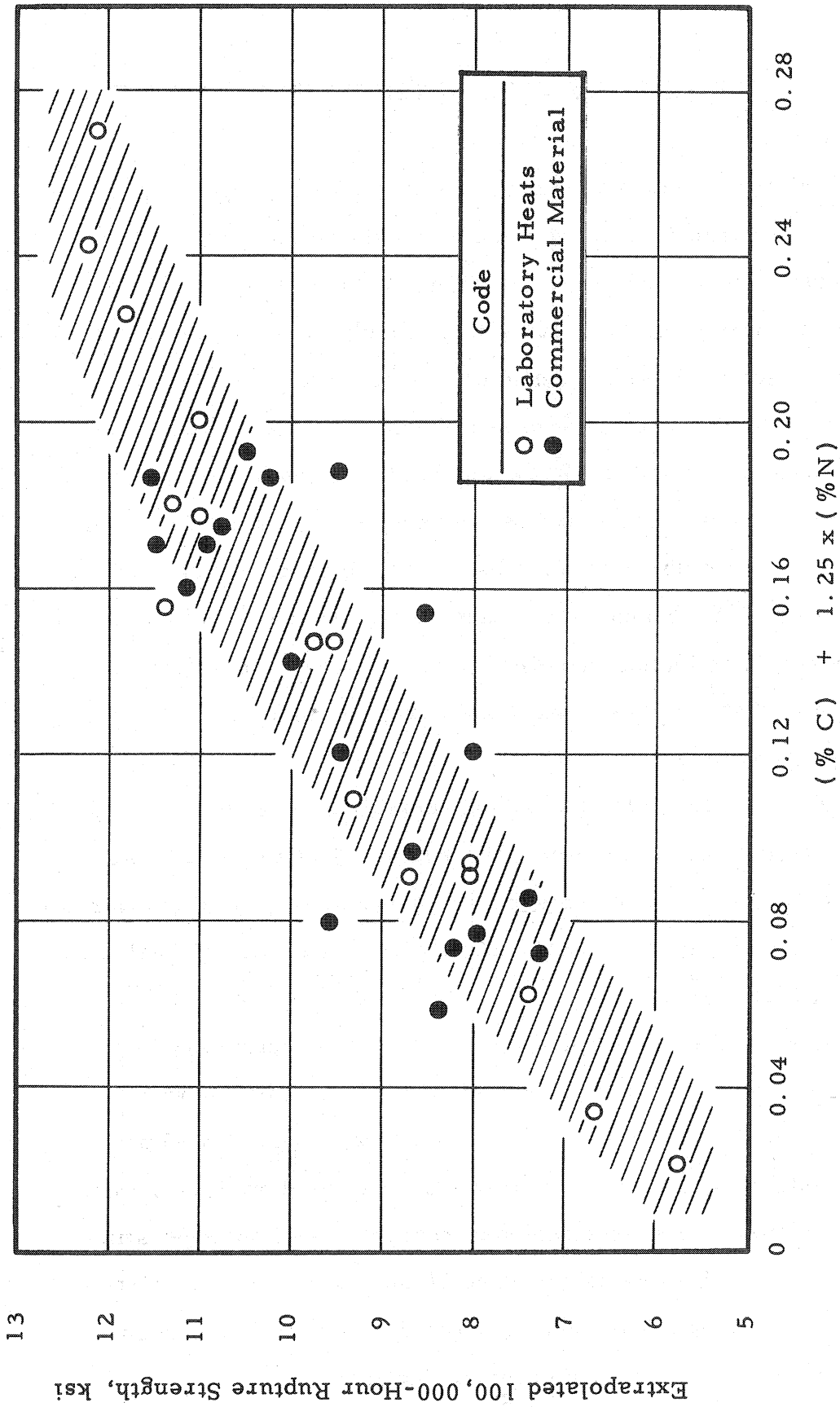
Figure 23. The influence of carbon and nitrogen on the 100,000-hour rupture strength of Type 304 austenitic steel at 1200°F, including data from laboratory and commercially produced material. The base composition of these materials was balanced so as to be wholly austenitic. All material was heat treated above 1800°F, but the history of the various materials prior to heat treatment is diverse. For further details, see Appendix C.

APPENDIX A

Special Creep-Rupture Tests

On the basis of the type of strengthening mechanism proposed by White and Freeman [2] a cursory effort was made to determine whether increased dislocation density, produced by cold working, could markedly alter the creep-rupture properties of Type 304 steel. In addition, it was intended to correlate the recrystallization behavior during testing with creep-rupture properties. In order to accomplish these objectives bars of Heat 1310A were solution treated at 2050°F, W.Q. and cold reduced by rolling 15, 25, 50 and 75 percent; bars from Heat 1282 were heat treated at 2050°F and cold reduced 25, 55 and 85 percent; a bar from the commercial tube PT-9 was heat treated at 2050°F and cold reduced 45%. These bars were sectioned and the resulting blanks machined into creep-rupture specimens.

The results of tests on these materials are given in Table A-I and can be summarized as follows:

(a) The specimens of Heat 1310A were appreciably strengthened at 1200°F by the 15 percent cold reduction. The rupture ductilities of these specimens were very low in comparison with material heat treated after cold reduction. These data are plotted along with that of the original material in Figure A-1.

(b) A specimen which had received 25 percent cold reduction also showed an increase in rupture strength at 1200°F over the solution treated material. The increase was not as great as resulted from 15 percent cold reduction. Microstructural examination showed that a considerable portion of this specimen had recrystallized during testing. The specimens which were cold worked 50 and 75 percent completely recrystallized during testing and as a result had drastically reduced rupture strengths and very high rupture ductilities.

(c) In the other materials (Heats 1282 and PT-9) considerable recrystallization occurred during testing at 1200°F when the amount of cold

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reduction was 25 percent or more. The rupture life of each of these specimens was reduced, compared with the solution treated specimens.

(d) Microstructural examination revealed that rather large amounts of sigma phase had formed in those specimens which recrystallized during testing.

It would be expected, based on other studies, [1, 51, 60] that cold reduction would increase the short time rupture strength. At some time period which is determined by the test temperature, a pronounced increase in slope of the stress-rupture curve should be noted which corresponds to the period in which recrystallization occurs. At time periods beyond that required for the completion of recrystallization, a marked decrease in the slope of the stress-rupture curve should occur. It would appear that the specimen of Heat 1310A, cold reduced 25 percent, ruptured in the transition stage between high and low strengths. The 15 percent cold reduced specimens, however, showed high strength. It is not known whether longer time tests would yield evidence of recrystallization with a corresponding loss of strength in the alloy cold reduced 15 percent. At the longer times sufficient recovery might be induced so that recrystallization will not occur. This is a matter for conjecture. These experiments have confirmed that small amounts of cold reduction, presumably by increasing the dislocation density, can increase the creep resistance of Type 304 steel.

In connection with the theories proposed by White and Freeman [2] for Type 321 steel, two tests were conducted on Type 304 steel to determine if the effect of the formation of a particular dislocation array (substructure) by prior creep exposure at one stress level could have any influence on the creep and rupture properties of the specimen at other stress levels. In Type 321 steel White and Freeman showed that such an exposure can have a marked effect.

These tests were conducted on a commercial material. The initial

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exposure was for 50 hours with a stress of 25,000 psi at 1200°F. The results are listed in Table A-I (compare specimens PT-9 - 1, 2, 3 and 4). To compare the rupture properties, the data should be corrected for the rupture life "used up" during the prior exposure. This can be accomplished using the "addibility-of-life-fraction" rule. The corrected rupture data and the creep rates are as follows:

Stress (psi)	Prior Exposure	Rupture Life (Hours)	Minimum Creep Rate (%/ 1 hour)
28,000	None	133	0.069
28,000	50 hours at 25,000 psi	122	0.108
22,000	None	1,047	0.0087
22,000	50 hours at 25,000 psi	1,091	0.0072

There was a slight change in the minimum creep rate due to prior exposure; at the high stress level the creep rate was increased by prior exposured and at the low stress level it was decreased. There were corresponding changes in the rupture properties. These changes, however, are insignificant. The conclusion resulting from these data is that in the absence of a strong precipitation reaction to "stabilize" a particular dislocation array, prior creep exposure does not markedly influence subsequent properties.

TABLE A-I

Summary of Special Creep-Rupture Tests

| Specimen No.	Heat Treatment °F	Test Temp. °F	Stress psi	Rupture Life hours	R. A. %	Elong. %	Min. Creep Rate %/hr.
PT9-1	2050	1200	28,000	133.1	28.0	20.4	0.069
PT9-2	2050	1200	22,000	1047.5	36.2	23.2	0.0087
PT9-3	2050	1200	25,000[a] 28,000	157.8	31.5	21.0	0.0240 0.1080
PT9-4	2050	1200	25,000[a] 22,000	1020.0	34.7	26.6	0.0245 0.0072
PT9-5	2050+45%CW	1200	22,000	196.1	28.3	14.7	
PT9-6	As received (37%CW)	1200	22,000	454.2	16.0	8.0	
PT9-7	2050	1200	20,000	20.1	43.7	33.1	
PT9-8	2050	1200	10,000	1803.3	28.5	24.6	
82-1	2050+25%CW	1200	15,000	508.6	8.7	8.2	
82-2	2050+55%CW	1200	15,000	71.2	59.4	46.7	
82-3	2050+55%CW	1200	20,000	28.0	59.2	42.6	
82-4	2050+75%CW	1200	15,000	25.9	80.7	72.6	
10A-1	2050+25%CW	1200	15,000	1100.9	57.2	33.1	
10A-2	2050+50%CW	1200	15,000	50.2	91.0	91.2	
10A-3	2050+75%CW	1200	15,000	12.9	95.3	76.7	
10A-4	2050+15%CW	1200	20,000	607.8	24.4	9.0	
10A-5	2050+15%CW	1200	15,000	3191.1	15.6	4.6	
10A-6	2050+15%CW	1200	25,000	4.8	48.5	20.4	

a - 50 hour exposure at 25,000 psi
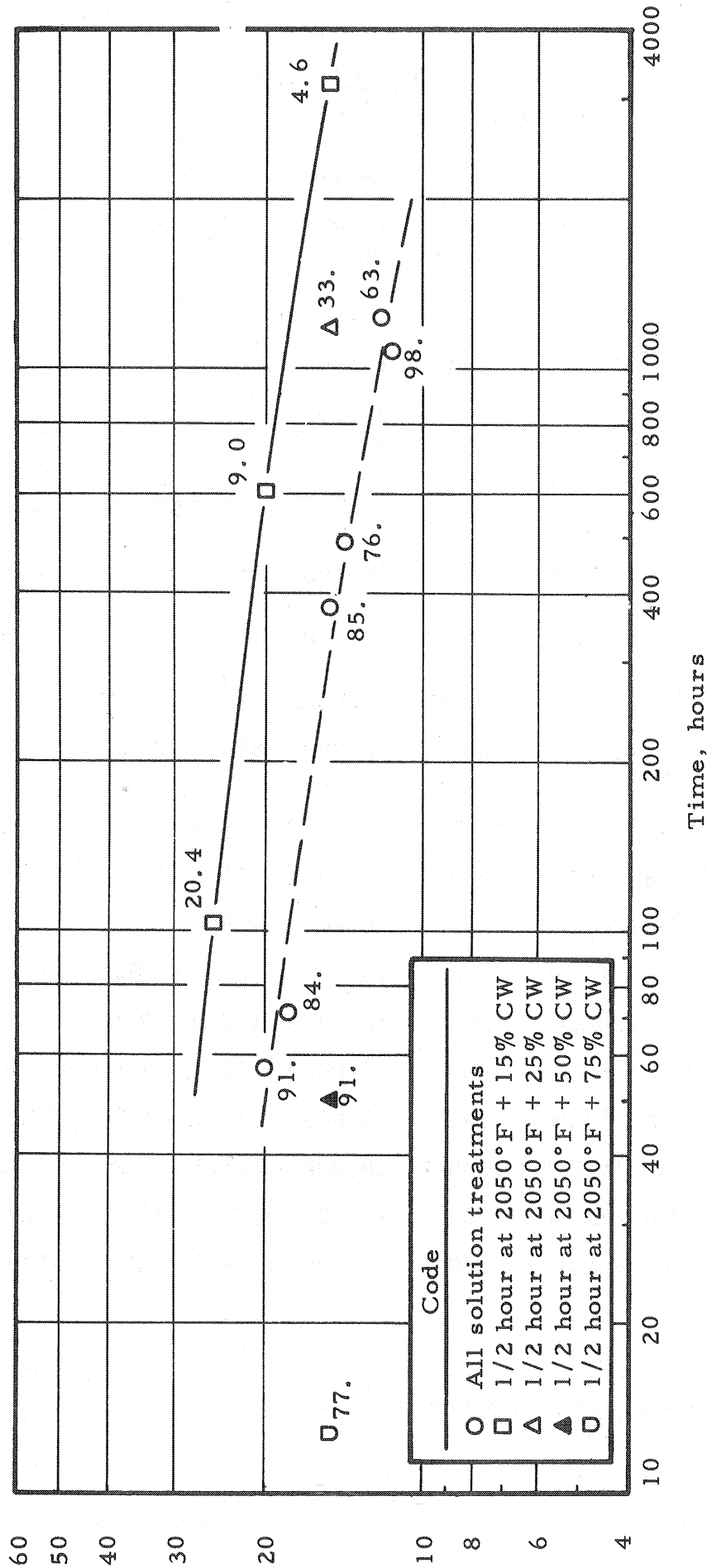
Figure A-1. Stress-rupture time curves at 1200°F for heat 1310A showing the effect of varying amounts of cold work. (The numbers after the symbols are elongations.)

APPENDIX B

Recrystallization

The recrystallization characteristics of several types of 18Cr - 10Ni base alloys have been determined. This study was undertaken to observe possible differences in recrystallization kinetics among related alloys, to aid in the understanding of the response of the alloys to various heat treatments and to provide a basis of comparison for materials believed to have recrystallized during testing or high temperature service.

Seven alloys were investigated, each with a specific compositional characteristic:

(a) Base alloy - low carbon and nitrogen - Heat 1310A.

(b) Normal carbon content, low nitrogen - Heat 1282.

(c) High nitrogen, low carbon - Heat 1343A.

(d) High nitrogen, normal carbon - Heat 1341A.

(e) Nitrogen, carbon, boron and titanium present - Heat 1339A.

(f) Very low manganese - Heat 1340B.

(g) Commercial tubing material - PT-9.

The alloys were solution treated at 2050°F and water quenched prior to receiving cold reductions of 15, 25 and 45 percent. Aging was carried out at 1200°, 1400° and 1600°F for times from one hour to 500 hours. Rockwell B hardness determinations were made on the specimens after aging and these measurements were plotted versus aging time. A curve of this type is shown in Figure B-1 for the commercial material (PT-9).

The time of the start of recrystallization (which was also determined metallographically) and the "time to half-hardness" were determined from the hardness versus time curves. The "time to half-hardness" is defined as the time at which the hardness is midway between the value at the start of recrystallization and the "final" hardness value after prolonged

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aging (completion of recrystallization and growth).* These values are tabulated in Table B-I. Measurements made on a commercial Type 321 alloy are also shown for comparison. Due to the difficulty of obtaining curves such as are shown in Figure B-1, the parameters in Table B-I should only be considered to be semi-quantitative.

Considering first the data for the commercial material PT-9, which are presented in Figures B-1 and B-2 and Table B-I, the following conclusions can be drawn:

(a) In comparison with Type 321 steel, the commercial Type 304 steel recrystallized rather rapidly. For instance, when cold worked 45 percent and aged at 1400°F, the time to half-hardness for tube PT-9 was less than ½ hour as compared with an estimated value of about 40 hours for the Type 321 alloy.

(b) The cold reduced commercial tube of Type 304 underwent some recrystallization at 1200°F. Recrystallization started between 10 and 50 hours at 1200°F in a sample cold reduced 45 percent. In a sample cold reduced 25 percent, some recrystallization was evident after 500 hours at 1200°F.

(c) The microstructural changes occurring at 1200°F in the cold reduced samples are characterized by the following sequence of events:

(1) Carbide precipitation at grain boundaries and slipped planes which is accompanied or followed by general "thickening" of the boundaries. This latter phenomenon was discussed in the section on Structural Examination.

(2) Recrystallization initiated at triple points and at grain boundaries in the form of irregularly shaped areas or patches. Some of the

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* This value, i.e. "the time to half-hardness", is simply a convenience parameter and does not necessarily represent a physically significant point such as the time at which "recrystallization" is half completed. Indeed, by the time the "half-hardness" point is reached, in most of the present work at temperatures of 1400°F or higher, there is a complete set of new grains (often irregularly shaped rather than equiaxed) throughout the structure. Whether or not this is to be referred to as completely recrystallized is a debatable point.

original carbide precipitates were visible within these areas under high magnification. Within the patches, concentration variations were evident and were apparently related to the concentrations gradients formed at the grain boundaries and at precipitate particles prior to recrystallization

(3) At somewhat longer times the boundaries of the small new irregular grains became visible and a new phase, probably sigma, formed in the recrystallized sections. The sigma phase, which was generally etched out by the 60 percent HNO_3 etch, appeared in a "worm hole" like pattern. This can be seen in Figure B-2b. The sigma phase was most frequently observed at the new grain boundaries. Lena and Curry[26] have also reported observing sigma phase in this form.

(4) At still longer times, the sigma phase was less apparent, the new grains grew somewhat and the boundaries of the new grains "thickened" slightly.

(d) The microstructural changes which occurred in the cold worked samples during aging at 1400°F were considerably different from those which occurred at 1200°F. The following sequence of observations was made:

(1) At 1400°F carbide precipitation on the cold worked structure was very intensive.

(2) Recrystallization at this temperature was characterized by the formation of new grains; first near the original boundaries (which, unlike the case at 1200°F, remained distinctly visible because of the precipitated carbide*) and then throughout the old grains. This appeared to occur uniformly throughout the sample, not in distinct patches as occurred at 1200°F.

(3) No sigma phase was apparent in this material after recrystallization at 1400°F.

* It should be noted that at low magnifications and when certain etchants were used, specimens such as those shown in Figure B-2 which were aged at 1400°F will show only the carbide precipitate in the pattern of the original cold worked structure. Recrystallization will not be evident under these conditions.

(e) At 1600°F the behavior during aging after cold working was very similar to that occurring at 1400°F, except that fewer carbides precipitated on the original cold worked structure prior to recrystallization. Some carbides also precipitated at the boundaries of the newly recrystallized grains.

For the other materials the recrystallization characteristics varied considerably, as can be seen in Table B-I. The values for the recrystallization parameters (i.e. the time to half-hardness and the time at which recrystallization started) for the material with low nitrogen levels were less than those for the material with high (>0.10 percent) nitrogen content. All of these values, however, were less than the values characteristic of Type 321 steel.

Where possible, the temperature dependence of the recrystallization parameters (the so-called recrystallization "activation energy") was estimated. Although this quantity is not very accurate there was no indication of any significant difference in this quantity between the different compositions. Furthermore, this quantity facilitated estimation of the recrystallization characteristics at higher temperatures. These estimates indicated that for all seven materials studied, the time to half-hardness was less than $\frac{1}{2}$ hour at 1750°F after about 25 percent or more cold reduction. Indeed, it appears that material with as much as about 45 percent cold reduction (which is common in the production of seamless tubing) will have reached the "half-hardness" point in less than $\frac{1}{2}$ hour at 1600°F (this can be seen in Figure B-1 for tube PT-9).

Careful re-examination of the microstructure of the commercial tubes of Type 304 steel used in the SP-6 investigation indicated that they had recrystallized during heat treatment at 1600°F. (In low magnification photomicrographs this fact can be easily missed.)

Some further information about the recrystallization and growth characteristics can be arrived at by comparing the variations in the grain size of the laboratory heats. These are given in Table B-II. The follow-

ing points are of particular interest:

(a) After solution treatment at 2050°F the heats which only had carbon additions showed an ASTM grain size number of approximately 2 - 3 regardless of the carbon content.

(b) After the 1750°F treatment the grain size tended to decrease with increasing carbon content, indicating that grain growth had been restricted by carbide precipitation.

(c) High nitrogen contents (about 0.10%) apparently had a restrictive effect on grain size. Lower nitrogen contents (about 0.05%), however, had little influence on grain size.

(d) There was no difference in the grain size of specimens of Heat 1343A (0.145%N, 0.02%C) heat treated at 2050°F and those heat treated at 1750°F.

(e) Titanium, at the 0.03 percent level, had only a slightly restrictive effect on the grain size in the absence of nitrogen during the 2050°F heat treatment, however, it was markedly restrictive when nitrogen was present.

This information, in the light of the findings, becomes of only secondary interest to the objectives of this investigation. The relevant conclusions will be summarized at this point, without further discussion. These conclusions are intended to apply specifically to material subject to the conditions which have been studied herein - this being that the material is in a well solution-treated condition prior to the cold working and aging. The conclusions are as follows:

(a) For all the Type 304 heats studied (the laboratory heats of this investigation and the production tubing material from the SP-6 investigation[1]), it was found that heat treatment of 25 percent cold reduced material for ½ hour at 1750°F was sufficient to result in a "completely"* recrystallized microstructure. The heat treatment of material cold reduced

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* That is, an entirely new grain structure. This does not necessarily mean that grain growth was completed or that the hardness had reached a minimum value.

approximately 40 percent for ½ hour at 1600°F had the same result.

(b) The combination of conditions leading to the recrystallization of Type 304 steel was somewhat less severe that those necessary to produce a similar tesult in Type 321 steel.

(c) Carbide precipitation, under certain conditions, could occur before recrystallization had annihilated the cold worked structure. This precipitate could (depending on metallographic technique) mask the recrystallized structure. This has not been found to happen in Type 321 steel.[1] The cause for this difference between the two steels is not presently understood.

(d) Carbide precipitation either before or shortly after recrystallization had a restrictive effect on grain growth.

(e) At 1200°F recrystallization apparently aided the formation of sigma phase.

Recrystallization Characteristics of Commercial Tube PT-9 and Several Laboratory Heats of Type 304 Steel and of a Commercial Type 321 Steel Tube

Reduction %	Temp. °F	Heat Number							Type 321
		1310A	1282	PT9	1343A	1341A	1339A	1340B	
		Time to half-hardness, hours*							
15	1200	>1000		>1000					
	1400	25		1000					
	1600	<.3		.5					
25	1200	800	350	>1000					
	1400	1.5	1	4-10	20	100	90	70	1100
	1600	<.2	<.3	.3	2.5	3	4	4	
45	1200			80					>500
	1400			<.4					40
		Time to start of Recrystallization, hours*							
25	1200	50-100	50-100	500					>500
	1400	.3-.5	.5	.5-1	10	40	50	30	50
	1600	.2	.2	.2	1-1.5	1.5	1-2	2	

*These parameters are derived from aging curves, and have the following meaning:

Time to half-hardness

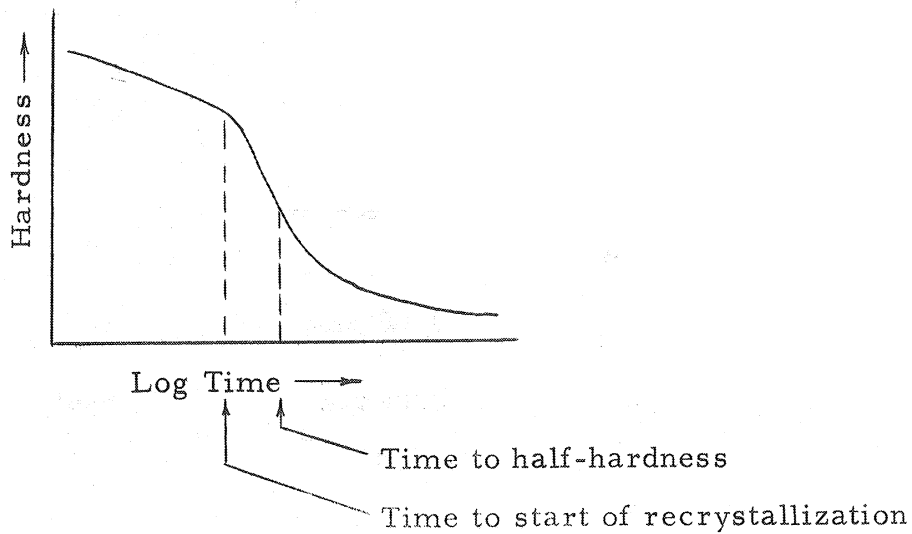Time to start of recrystallization

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TABLE B-II

ASTM Grain Size of Some Laboratory Heats after Heat Treatment at 2050°F and 1750°F

| Heat No.	Composition Variables, %				Grain Size	
	C	N	Ti	B, ppm	2050°F	1750°F
1310A	0.009	-	-	-	3	6
1338A	<0.02	-	0.03	15	5	-
1282	0.06	-	-	-	2-3	8
1357A	0.05	-	-	-	1-2	5-7
1312	0.14	-	-	-	3	9
1361A	0.03	0.06	-	-	1-2	-
1343A	0.02	0.145	-	-	6	5-6
1362A	0.07	0.06	-	-	2-3	-
1341A	0.06	0.08	-	-	5	7-8
1344A	0.06	-	0.035	-	4-5	-
1344B	0.06	0.12	0.035	-	8	-
1337A	0.06	-	0.03	15	3-4	-
1361B	0.03	0.07	0.03	15	3-4	-
1338B	<0.02	0.13	0.03	15	7	6-7
1339A	0.07	0.124	0.03	15	7-8	6-7
1362B	0.16	0.13	0.025	15	4-5	-
PT9	0.05	0.09			3-4	8
1340A	0.01	0.12	0.08 Mn		3-4	-
1340B	0.04	0.13	0.08 Mn		5-6	-
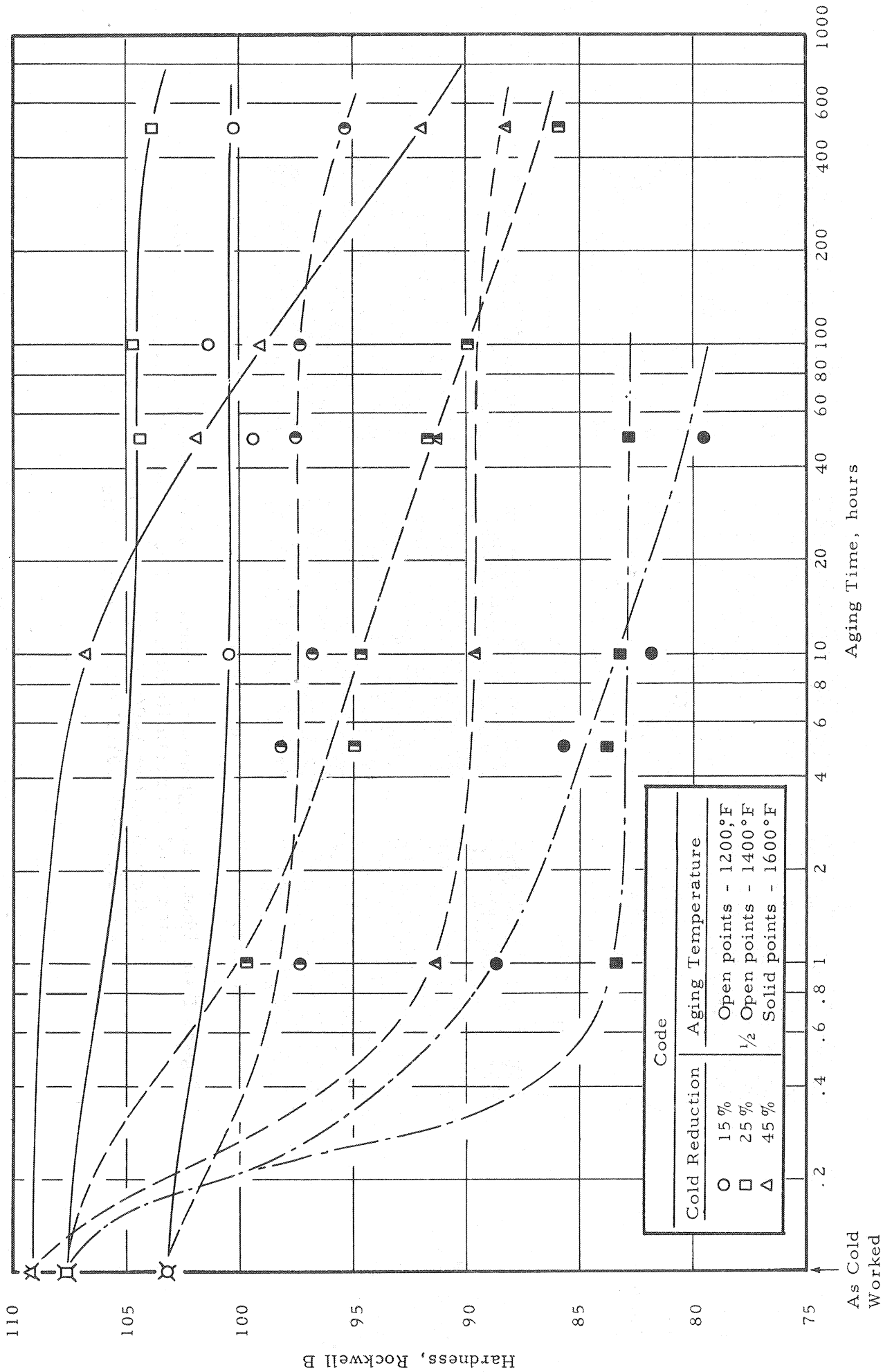
Figure B-1. Aging curves at 1200°, 1400°, and 1600°F for commercial tube PT-9, cold worked 15, 25, and 45 percent in cross-sectional area.

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Cold
Reduced
45%
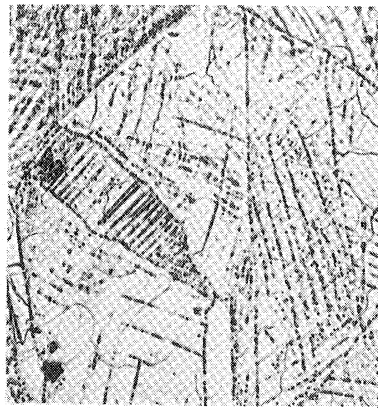
Aged at
1200°F
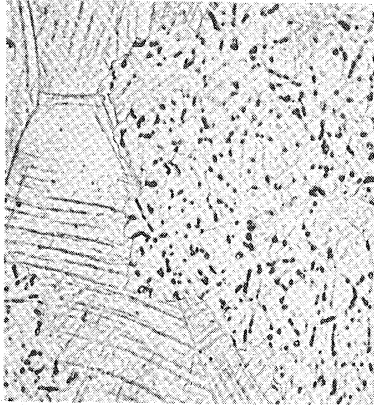
a) 50 hrs. b) 100 hrs. c) 500 hrs.

Cold
Reduced
25%

Aged at
1400°F

d) 10 hrs. e) 50 hrs. f) 500 hrs.

Figure B-2. Photomicrographs of a commercial material, PT-9, at various stages of recrystallization at 1200°F after 45 percent cold reduction and at 1400°F after 25% reduction. Etched electrolytically with 60% HNO_3. Magnification - 500X

APPENDIX C

The influence of carbon and nitrogen on the estimated 100,000-hour rupture strength of Type 304 steel.
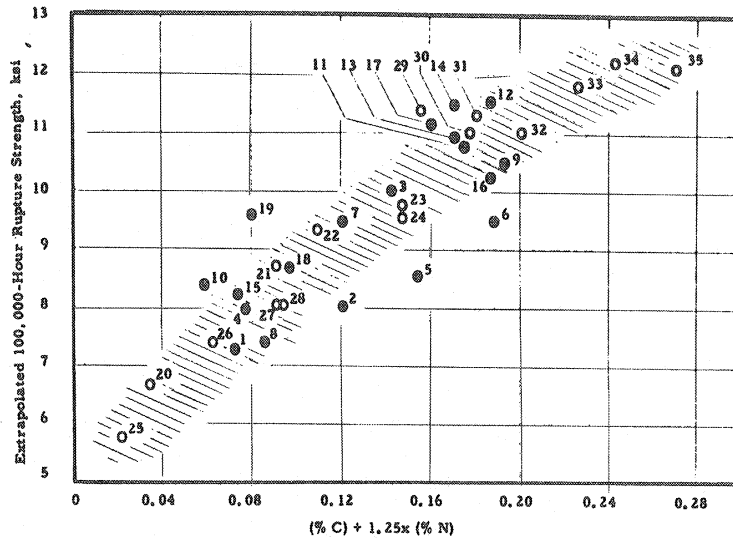
Data Point No.	Chemical Composition, percent						(%C) + 1.25x(%N)	Type of Working	Heat Treatment °F	100,000-hr. Rupt. Strength psi	Ref.
	C	N	Mn	Ni	Cr	Si					
1	.032	.036	.07	10.92	18.68	(.25)[a]	.073	H.R.[b]	2000	(7.2)[c]	30[d]
2	.067	.042	.16	11.18	18.28	(.25)	.12	H.R.	2000	(8.0)	30[d]
3	.104	.039	(.10)	10.97	18.28	(.25)	.153	H.R.	2000	(10.0)	30[d]
4	.036	.034	(<.1)	10.20	18.57	(<.1)	.078	H.R.	2050	(8.0)	19
5	.030	.10	1.47	9.72	19.13	.64	.155	H.R.	1975	8.5	28
6	.025	.13	1.63	9.87	18.87	.55	.188	H.R.	1975	9.5	28
7	.070	.04	1.62	9.51	18.88	.79	.12	H.R.	1975	9.5	28
8	.05	.028	.53	10.7	18.5	.61	.84	H.R.	1900	7.3	59
9	.018	.14		11.3	19.2		.193	-	1950	(10.5)	59
10	.018	.032		11.3	18.9		.058	-	1950	(8.5)	59
11	.052	.10	1.66	10.40	18.47	.55	.177	H.R.	1950	10.8	6
12	.059	.10	1.69	10.33	19.67	.47	.184	C.R.	1950	11.5	6
13	.050	.10	1.64	10.45	18.86	.37	.170	C.R.	1950	(11.0)	6
14	.057	.096	1.63	10.61	19.15	.48	.170	H.R.	1950	(11.5)	6
15	.02	.045	1.10	10.56	18.55	.32	.076	-	1950	8.2	-
16	.026	.13	1.12	9.48	18.19	.34	.188	H.R.		10.2	-
17	.054	.082	1.78	10.41	19.09	.48	.160	C.R.	2050	11.2	1
18	.06	.028	1.35	10.50	18.56	.69	.095	C.R.	2050	8.2	1
19	.04	.031	1.42	10.00	18.45	.50	.079	C.R.	2050	9.5	1
20	.022	(.01)	1.47	10.36	18.08	.48	.034	C.R.	1950	6.7	1[d]
21	.083	(.01)	1.50	12.63	17.78	.71	.095	C.R.	2050	8.9	1[d]
22	.096	(.01)	1.59	10.54	18.09	.48	.108	C.R.	2050	9.3	1[d]
23	.087	.049	.61	10.54	18.77	.40	.148	C.R.	1950	9.7	1[d]
24	.090	.046	2.06	10.06	18.46	.47	.147	C.R.	1950	9.4	1[d]

Laboratory heats from this investigation:

Point No.	Heat No.	Point No.	Heat No.
25	1310A	31	1362A
26	1357A	32	1343A
27	1361A	33	1342B
28	1360A	34	1341B
29	1343A	35	1343B
30	1341A		

a - Composition values in parentheses are estimated.

b - Type of working prior to heat treatment:
  H.W. - hot reduced
  C.R. - cold reduced

c - Extrapolated 100,000-hour rupture strength. Values in parentheses are derived from data of less than 500 hours duration.

d - Small scale laboratory heat