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A STUDY OF THE FUNDAMENTALS OF THE EFFECT OF DEOXIDATION ON THE CREEP CHARACTERISTICS OF PLAIN CARBON STEEL

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A STUDY OF THE FUNDAMENTALS OF THE EFFECT OF DEOXIDATION ON THE CREEP CHARACTERISTICS OF PLAIN CARBON STEEL

by Clayton Dale Dickinson

The relationship between the creep strength and dissolved nitrogen in plain carbon steels was studied in order to explain the wide variation in the reported creep strength for plain carbon steels with different deoxidation practices and heat treatments.

This relationship between nitrogen and creep rate was studied for a group of commercial plain carbon steels which were representative of the range of rimmed, silicon and aluminum deoxidation practices for plain carbon steel. A specially prepared group of vacuum melted and air melted steels were also tested.

The creep rates of the steels were determined for the 500 to 600 hour interim at 850° F. and 15,000 psi. The dissolved nitrogen was determined by the difference between the values for the total nitrogen and the nitrogen in the form of nitrides in the steel. The amount of dissolved nitrogen in the steels was changed by varying the heat treatment or processing prior to the creep tests.

For the heat treated deoxidized steel, the logarithm of the creep rate showed a very significant linear decrease with an increase in the amount of nitrogen in solid solution. The deoxidation practice and heat treatment had no real effect on the creep rate except for the effect of these processes on the nitrogen in solid solution in the steel.

The logarithm of the creep rate of rimmed steels was found to decrease linearly with an increase in total nitrogen; however, the rate of increase in strength from nitrogen is not as great for rimmed steels as for deoxidized steels.

Hot rolling, stress relieving and spheroidizing processes were found to cause a change in the amount of nitrogen in solid solution in the steel. The creep rate of both silicon and aluminum killed steels was related directly to the amount of nitrogen retained in solid solution after these treatments.

Removal of nitrogen by vacuum melting or vacuum annealing caused the creep rate to increase to the same degree as the removal of nitrogen by the precipitation of nitrides.

No consistent relation was found which related creep rate with austenitic grain size, microstructure or hardness. The level of creep rate increased with manganese in the range of 0.00 to 0.82 percent for a narrow range of low dissolved nitrogen. However, increased dissolved nitrogen further decreased the creep rate at all manganese levels.

The relation between creep rate and dissolved nitrogen consistently explained the effect of deoxidation and prior processing on the creep strength. Silicon deoxidized steels have high creep strength in most conditions of heat-treatment because the nitrogen is dissolved and retained in solid solution by these treatments. The nitrogen in fully deoxidized aluminum killed steels is precipitated as aluminum nitride for most heat treatments. Heat treatments which improve the creep strength of aluminum killed steels also increase the dissolved nitrogen. Rimmed steels are strengthened by nitrogen, but the absence of silicon or aluminum in the steel to interfere with the movement of the nitrogen atoms, reduces the strengthening effect of nitrogen in rimmed steels at temperatures above about 600° F.

Nitrogen increased the strength of steel only under conditions which involve plastic deformation. A modification of Cottrell's strain aging mechanism offers the best explanation for this behavior.

I

INTRODUCTION

A major source of variation in creep strength exists in plain carbon steels and low alloy steels as a result of variation in the degree and type of deoxidation and heat-treatment. However, the mechanism for the effect of deoxidation and heat-treatment is not fully understood. This study was conducted to test the proposal that the change in creep strength with deoxidation and heat-treatment resulted largely from the effect of these processes on the nitrogen in solid solution in the steel. It was further proposed that there would be a correlation between the dissolved nitrogen and the creep strength which would explain the gross changes in creep strength in spite of minor variations which might result from differences in prior treatment. The object of this study is to test the extent of the correlation between nitrogen and the creep strength and to propose a mechanism to explain this correlation.

The magnitude of the effect of the variation in high temperature strength with deoxidation varies considerably with stress and testing temperature, but has a very significant effect in the range of temperature and stress at which plain carbon steel is most widely used for high

temperature service. For plain carbon steels in the normal range of composition, stresses from 6,000 psi to 18,000 psi have been reported for a creep rate of 1×10^{-5} percent per hour at 800° F.(1, 2). These figures are only typical values and the variation in strength is proportionally as great at other temperatures. Deoxidation and heat-treatment are not the only factors which control the creep strength, and even the type of melting furnace has been shown to influence the high temperature strength. The variation in strength from the interrelated factors of deoxidation and heat-treatment is much greater than the effects of other manufacturing variables. However, there is no one heat-treatment or deoxidant which will universally yield high or low creep strength, and it will later be shown that neither factor is the fundamental cause of the large variation in creep strength.

Creep strength is only one of many variables or properties of steels which are affected by deoxidation practice and heat-treatment. The type and degree of deoxidation are known to cause a variation in the austenite grain size of most steels. Differences in the response to heat-treatment and in the final properties of the steels in many cases seem to parallel the grain size variation. Rimmed and silicon-killed steels have low coarsening temperatures and, as a result, exhibit fairly large austenitic grain sizes when heated to normal austenitizing temperatures. Fully killed aluminum-deoxidized steels have high coarsening temperatures and a fine austenitic grain size is obtained with normal heat-treatment operations. In addition, the microstructure and particularly the carbide distribution differ for steels with various deoxidation and heat-treatment histories. The simultaneous variation of carbide distribution, austenitic grain size, and creep strength has led to the belief that differences in the creep strength were caused by these factors. Later studies determined that the variations between grain size and creep strength were only manifestations of the same basic changes which resulted from variations in deoxidation practice and heat-treatment (3). As a result of this work, a mechanism was proposed based on the solution and precipitation of an unknown product of deoxidation, presumably oxides. However, this mechanism has not been verified experimentally and is, in fact, in conflict with the thermodynamics involved in the deoxidation process.

Beeghly (4) has developed a method of chemical analysis for aluminum nitride which has been applied very successfully in the study of mechanisms for the effect of deoxidation on many properties such as austenitic grain growth, graphitization, strain aging at room temperature, strain embrittlement and strain induced recrystallization. Beeghly's method of analysis permits a new approach to the problem of the effect of deoxidation on creep strength of plain carbon steels and should provide information which will lead to a better understanding of the mechanism for these effects.

As a matter of fact, as this study was being completed, Bardgette (5) reported that there was a correlation between the creep strength of plain carbon steel and the aluminum precipitated as aluminum nitride, as shown by Beeghly's method. Since the total nitrogen remains constant for a given steel, it is apparent that there is also a correlation between the creep strength and the dissolved nitrogen as proposed in this study. Therefore, although Beeghly's method of analysis offers a key to the effect of deoxidation on the creep strength, the meaning of the correlation between the nitrogen or aluminum nitride and the creep strength must be studied before the basic mechanism can be evolved.

A thorough study of the investigation of the mechanism for the effect of deoxidation on the creep strength of plain carbon steel is justified because the basic mechanism should have much broader application. At the present time, this factor of major importance in the creep and rupture strength of plain carbon steels, is not adequately explained. It is quite probable that a factor of such importance in the high temperature strength of plain carbon steel could also be involved in the strengthening of many other high temperature materials. Equally significant is the fact that such gross effects from a source which is not thoroughly understood could mask some of the effects of alloying elements, such as chromium, molybdenum, vanadium, carbon, etc. Therefore, before the effect of various alloying elements can be evaluated exactly, this source of uncontrolled variation must be understood.

The purpose of this investigation is to determine whether there is a correlation between the creep strength and the change in the amount of precipitated or dissolved nitrogen, as shown by Beeghly's method. In addition, the processes which could influence the creep strength will be examined in order to explain the large variation in creep strength now attributed to deoxidation.

II

REVIEW OF THE LITERATURE

Effect of Deoxidation and Heat-Treatment

The effect of manufacturing variables and particularly deoxidation variables on the creep strength of plain carbon steels is fairly complex and has received much attention. The creep strength of mild steel is sensitive to prior history, and even the type of melting furnace has been found to influence the creep strength. Steels which have been produced by the Bessemer process or melted in an electric arc furnace generally exhibit higher creep resistance than steels made by either the acid or the basic open hearth method. The magnitude of this effect, however, is dwarfed by the range of creep rates reported for steels with varying deoxidation practice, and this variable has received even more attention. The deoxidation variable is further complicated by the effect of subsequent heat-treatment and, in particular, austenitizing temperature. The variation of creep strength with heat-treatment, furthermore, has been shown to be dependent on the type and degree of deoxidation so that the important factor is believed to be deoxidation.

Investigations into these effects have been quite thorough so that certain generalizations are possible

(3, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14). Silicon killed steels, for example, have high creep strength in almost all conditions of heat-treatment regardless of austenitizing temperatures or cooling rate (3, 8, 9). At temperatures above 800° F., the strength of rimmed steel is much lower than that of silicon-killed steels, and again the strength is relatively independent of prior heat-treatment (7). Also, the creep strength of the core of a rimmed steel is stronger than the rim material (8). Aluminum-killed steels which have been deoxidized with minor amounts of aluminum (up to about 1.5 pounds per ton) generally possess creep strengths similar to that of silicon-killed steels.

The amount of aluminum added per ton of steel is a poor criterion for determining the limit for high strength, and it has later been shown that there is some relation between the creep strength and the amount of soluble or metallic aluminum remaining in the steel after deoxidation (5, 6). Steels, which have been deoxidized with aluminum in amounts greater than two pounds per ton or with high residual aluminum, are generally considered to have low creep strength in most conditions of heat-treatment. It has been shown, however, that these steels have creep strengths as high as that of silicon-killed steels after they have been austenitized above the coarsening temperature and air cooled in reasonably small sections. The literature also indicates that these steels possess high creep strength in the as-rolled condition regardless of deoxidation practice (12, 13). Air cooling aluminum-killed steels from a fine grain austenite or furnace cooling from either the coarse or fine grain austenite results in a steel with a considerably reduced creep strength. The above generalities are not universal, however, as shown by the results obtained from a non-aging steel by Cross (9). The creep strength of this steel was not improved by coarsening and air cooling, and it was necessary to water quench from above the coarsening temperature in order to improve the creep strength of this very high aluminum-deoxidized steel.

Although most of these studies were conducted on steels with 0.10 to 0.20 percent carbon, the effect of deoxidation is not limited to this carbon range or to plain carbon steels. Steels containing as high as 0.35 percent carbon also exhibit the same variation with deoxidation and heat-treatment (3). Deoxidation has also been shown to cause changes in creep strength of specially prepared steels with carbon in the range of 0.006 percent. Steels with up to 0.5 percent molybdenum also exhibit wide variations in creep strength as the result of deoxidation and heat-treatment, and there is every indication that the effect of deoxidation is important in other low alloy steels (15, 16, 17, 18, 19).

The reasons leading to the attempts to develop a mechanism based on the relation between austenitic grain sizes and the resulting creep strength can easily be seen upon the examination of the effects of aluminum deoxidation on the grain size at various levels of added aluminum. Silicon-killed steels to which no aluminum has been added generally have a very coarse austenitic grain size at 1700° F. (20, 21, 22, 23, 24, 25). Aluminum additions up to about 1.5 pounds per ton cause little or no change in the grain size and the resulting creep strengths are as high as those of the silicon-killed steels. Additions of 1.5 to 2 pounds per ton of aluminum as a deoxidant can result in either fine or coarse grained austenite, and steels with this range of added aluminum may even exhibit a mixed grain size in which both coarse and fine grains exist side by side. Both high and low creep strength materials have been reported for steels with this range of aluminum addition. Steels deoxidized with greater than two pounds of aluminum per ton exhibit a fine grain size at 1700° F., and the creep strength of these steels is generally low in most conditions of heat-treatment. These same steels, air cooled from temperatures which result in a coarse austenitic grain size, exhibit creep strength as high as the inherently coarse grained materials.

Grain size has been shown to affect the creep strength of many nonferrous materials, and the phenomenological conclusion is that the austenitic grain size affects the creep strength of the steel. A mechanism for the effect of austenitic grain size on the creep strength of the steel could be evolved if it were not for the fact that the material is tested in the ferritic condition. To further complicate such a mechanism, the ferritic grain size is relatively independent of austenitic grain size and more dependent on cooling rate with the slower cooling rate or high transformation temperatures resulting in larger ferritic grain sizes.

However, Cross (3, 8, 9, 10) concluded that neither grain size nor microstructure were involved in the effect of deoxidation from the following results: A silicon killed steel which was heated to either a low or high austenitizing temperature and air or furnace cooled had high creep strengths which were the same within the accuracy which can be expected between two creep tests. An aluminum-killed steel with the added aluminum in the range of two pounds per ton had high creep strength only when cooled fairly rapidly from above the coarsening temperature. Furnace cooling the coarse austenitic grains resulted in creep strengths as low as found for the fine grained condition of this material. The austenitic grain size of all four coarsened samples was uniformly large and, therefore, all of the steels should be strengthened by the effect of austenitic grain size if such effect existed. The slowly cooled steels would have the largest ferritic grain size and would be expected to be strengthened if the ferritic grain size was a factor. This, of course, was not the case and, therefore, the effect of deoxidation could not be directly connected with the grain size.

Of course, there are differences in microstructures between the air and furnace cooled samples. The coarsened air cooled samples had a Widmanstätten structure and the microstructure of the furnace cooled samples consisted of coarse lamellar pearlite. However, the creep strength of the silicon-killed steel with the coarse lamellar pearlite is as high as that of the same steel in other conditions of heat-treatment so that microstructure and/or carbide distribution could not be the major factor involved in the effect of deoxidation. This led to the conclusion that the similarities between austenitic grain size variations and creep strength are not related directly but are manifestations of some more fundamental mechanism involving the deoxidants or products of deoxidation.

This conclusion was supported by comprehensive study of the effect of deoxidation and heat-treatment on the creep strength of plain carbon steels. As a result of these studies, a mechanism was proposed based on the Dorn and Harder mechanism for grain growth of carbon steels which had developed at that time (23). According to Dorn's mechanism, steels which had been deoxidized with excess aluminum did not exhibit grain growth at normal austenitizing temperatures because of the formation of a film or network of some product of deoxidation which inhibited grain growth. Increasing the austenitizing temperature resulted in the solution of this network in some regions which resulted in a duplex grain size at temperatures just below the coarsening temperature (24). The same nonuniform solution of the grain boundary network could be used to explain the mixed grain sizes found by the McQuaid-Ehn test for some steels which had been deoxidized with aluminum in the range of 1.5 to 2 pounds per ton. It has since been shown that continuous envelopes are not required for grain growth inhibition and grain growth can be prevented by fine precipitates distributed in the grain boundaries. With these modifications, the generally accepted mechanism for grain growth inhibition in aluminum-killed steels has been evolved from the basic concepts set forth by Dorn and Harder.

An explanation of the effect of heat-treatment and deoxidation on the creep strength was developed from this hypothetical solubility with the assumption that the unknown, "X", was aluminum oxide (8). Cross proposed that the silica in silicon-killed steels was dissolved in the austenite at almost any austenitizing temperature and, on cooling, remain in supersaturated solution to precipitate as submicroscopic particles. These particles interfered with slip and greatly reduced the creep rate. Rimmed steels were weak according to this mechanism because they contained no silica to precipitate on cooling. The high creep strength of steels which had been deoxidized with silicon and minor additions of aluminum was explained on the basis that there was still sufficient silica to produce high creep strength in most conditions of heat-treatment. The low creep strength of aluminum-killed steels, which had a fine McQuaid-Ehn grain size, was attributed to the formation of "X" (aluminum oxide or aluminum silicates in silicon-aluminum-killed steels) in these steels. According to this mechanism, the aluminum oxides precipitated at the grain boundary of the newly formed austenite as the steel passed through the critical region. With normal austenitizing procedure carried out below the coarsening temperature of the steel, the aluminum oxide remained in the grain boundaries and agglomerated into large precipitates which could not interfere with the creep process. As the austenitizing temperature of the steel was increased above the coarsening temperature, the aluminum oxide was dissolved in the austenite and, with fairly rapid cooling rates, remained in solid solution and precipitated as submicroscopic inclusions similar to the silicon-killed steels.

In silicon-aluminum-killed steels, the oxygen was assumed to be present in the form of aluminum oxide or complex aluminum silicates which have the same solubility as the oxides in the aluminum-killed steels. Thus, the change in strength with heat-treatment of these steels is explained on the same basis that was proposed for the aluminum-killed steels. In rimmed steels, no oxides of deoxidants are present and the iron oxide in the steel was precipitated by any condition of heat-treatment in a form which does not improve the creep strength.

Cross' comprehensive study of the effect of deoxidation did much to define the interrelated effects of heat-treatment and deoxidation on the creep strength of ferritic materials. However, the mechanism presented to explain these effects was necessarily hypothetical, based on the solution and precipitation of oxides of aluminum or silicon. Solution and precipitation of aluminum oxide in the solid state is hardly possible since this material is only slightly soluble in the liquid. In addition, oxygen in iron has been shown to have a solubility of less than 0.003 percent over the entire austenitic region (26). More recently, it has been shown that aluminum nitride is dissolved above the coarsening temperature to permit austenitic grain growth in aluminum-killed steels. Therefore, aluminum nitride is the "X" of the Dorn-Harder mechanism. Since it is possible to measure accurately the solution and precipitation of this element with heat-treatment, it should now be possible to understand the more basic factors involved in the effect of deoxidation on the creep strength.

Many recent investigations have confirmed Cross' experimental results and have added much to the knowledge of the effect of deoxidation. However, the variation in the microstructure and austenitic grain size is still considered to be an important factor by some authors.

Effect of Other Manufacturing Variables

Steels produced in an electric furnace were shown to have higher creep strength than basic open hearth steels in one of the first investigations on the effect of manufacturing variables on creep strength (7). More recently, several comprehensive studies were conducted on the combined effects of melting furnace and deoxidation variables (12, 14, 19). The effect of melting furnace variation, including acid open hearth, basic open hearth, electric furnace, and the Bessemer process, was studied for steels with varying degrees of deoxidation by relatively short-time creep tests (12). The steels were tested in the as-rolled condition and after normalizing at about 1650° F. Little significant difference was found in the creep strength of the steels in the as-rolled condition. The creep strength of the normalized steels, however, depended very markedly on the type and degree of deoxidation. The majority of the tests in this study were run at 17,900 psi at 450° C. (842° F.). However, additional tests conducted at 400° C. and 550° C. (752° F. and 1022° F., respectively) indicated the same order and magnitude of creep strength differences existed at these test temperatures.

Smith and Dulis (14) studied the effect of the type of melting furnace and deoxidation on the strength of carbon steels. The steels were tested by creep and rupture tests at 850° F. after normalizing at 1650° F. Bessemer steel was shown to be superior to open hearth steel in the rimmed or capped condition but no difference between melting furnaces was found for the creep strength of fully killed aluminum deoxidized steels.

Fully killed aluminum deoxidized steels and rimmed steels were found to have inferior creep and rupture strength at 850° F. Steels which had been deoxidized with silicon and with minor additions of aluminum or titanium had superior strength at this temperature. It was concluded that the reported wide variation in the creep strength of carbon steels was related to variation in deoxidation practice and other differences in prior history. Although no mechanism was presented to explain these effects, it was also concluded that, once the basic cause of these variations was recognized, it would be possible to produce materials which had more uniform high temperature strength.

The effect of deoxidation on the creep strength of plain carbon plate and pipe steels in the as rolled or as rolled and stress relieved conditions was reported by R. F. Miller (13). The results of this investigation were very interesting, particularly so since two of the steels tested in the present study were obtained from these commercial heats. No difference between the rupture strength of these steels was found at 1000° F. even for rupture times of 9,600 hours, and the pipe steels had similar creep strengths for the stresses considered, regardless of deoxidation. However, the plate steels had been stress relieved as is generally the practice for this grade of material, and the silicon-killed steels had superior creep strength at lower stress levels. The strain aging peak at 400° F. was not observed in the stress-relieved aluminum-killed steels but was very pronounced for the tensile tests of the as rolled and stress relieved silicon-killed steels. Beeghly's method of analysis indicated that stress relieving had caused precipitation of some of the aluminum nitride, and this precipitation was apparently responsible for the reduction in strain aging tendencies.

In the discussion (27), it was pointed out that, in the range of stress of from 2,000 to 4,000 psi, both the silicon and aluminum-killed steels showed erratic behavior in creep which resulted in alternately high and low creep strengths as the test progressed.

In the final stages of the present investigation, a relation between the creep strength and the soluble aluminum or the aluminum precipitated as aluminum nitride was reported by Bardgette (5). The results indicated that steels containing more than 0.015 percent aluminum as metallic aluminum could be expected to exhibit poor creep strength. In addition, a more precise correlation was developed between the aluminum present as aluminum nitride and the creep strength variation. It is now generally accepted that aluminum nitride is the grain growth inhibitor and therefore determines the austenitic grain size of the steel. It was concluded that the loss in creep strength from aluminum deoxidation was due to the precipitation of aluminum nitride in those steels, which inhibited grain growth and caused a very fine austenitic grain size. It was further shown that, as a fine grained steel was heated above the coarsening temperature, the aluminum nitride was dissolved and the creep strength increased.

Although the solution and precipitation of nitrogen (and as a correlate aluminum nitride) is believed to be the basic factor involved in the variation of creep strength with deoxidation practice, a mechanism which depends on the growth of austenite for improved creep strength is not in agreement with the relations first developed by Cross' investigation.

The status of the effect of deoxidation on creep strength is thus very complex today. Several popular theories have been and are still being presented which relate the change in creep strength by deoxidation to such factors as microstructural and austenitic grain size differences. In addition, a mechanism for strengthening, involving the critical dispersion of submicroscopic precipitates, has been proposed. It has also been shown that the tendency towards spheroidization is increased by strong deoxidation with aluminum (28), and the effect of this process on the creep strength should be examined. Another mechanism which has not been proposed to date could be developed based on the effect of deoxidation on the dissolved or soluble nitrogen and the subsequent effect of this state on the strain aging tendencies of the steels. This basic concept was examined carefully so that its effect on both the room and elevated temperature properties of the steel was understood, and a brief synopsis of Cottrell's theory for strain aging under creep conditions follows.

Description of Strain Aging Phenomena

A large number of diverse phenomena are peculiar to plain carbon steels and a few other commercial materials. Among these are the yield point, strain aging, serrated stress-strain curve, and the increase in ultimate tensile strength to a maximum value in the range of 400° F. These seemingly diverse phenomena are all closely related in that they occur primarily in materials which contain interstitial elements in solid solution. Cottrell has developed a theory which explains the function of the interstitial solid solution elements in these phenomena (29), and recently, he extended this mechanism to include the effect of strain aging on the creep strength at low and high temperatures (30).

The effect of interstitial elements on the room and slightly elevated temperature properties has been verified, in many cases, by experimental evidence. For steel, it has been found that nitrogen is, perhaps, the more important element involved in strain aging phenomena, and that the removal of nitrogen from solid solution, either by precipitation or by complete elimination, results in the disappearance or decrease of many strain aging phenomena. The following discussion of the mechanics of Cottrell's theory is presented in terms of the special case of nitrogen dissolved in iron.

Nitrogen dissolved in interstitial solid solution causes a very large strain in the crystal lattice. The lattice contains imperfections such as grain boundaries and dislocations and the nitrogen in solution around these imperfections not only results in less distortion of the crystal lattice but effectively reduces the strain of misfit at the edge of the dislocation. The overall internal energy is substantially reduced if the nitrogen atoms are grouped as "atmospheres" around the dislocations in the metal. Since a dislocation which has an atmosphere of dissolved nitrogen surrounding it is at a lower energy state, the strain energy necessary to move the dislocation is increased. The stress, therefore, to cause plastic deformation is increased due to the increased energy required for plastic deformation.

At room temperature, plastic deformation of plain carbon steels takes place catastrophically, which gives rise to the upper and lower yield point frequently observed for carbon steels. Steel behaves elastically for all practical purposes up to the upper yield point after which there is a sudden drop in load. Subsequent plastic deformation proceeds in a discontinuous manner at a lower and almost constant stress. This phenomenon is explained by the theory that the dislocations, which have been surrounded by atmospheres of nitrogen atoms, cannot be moved until a critical stress is reached. Once this stress has been reached, a few dislocations break free from the atmospheres of nitrogen and move through the crystal lattice. As these dislocations pass other "trapped" dislocations, they impart sufficient energy to remove the "trapped" dislocations from the atmospheres of nitrogen. This results in a chain reaction which permits catastrophic plastic deformation at a much lower stress than originally required.

Another phenomenon involved in strain aging is the return of the yield point. A steel which has been deformed past the yield point and tested immediately will show a simple stress-strain curve with no yield point. The same steel, which has been aged for several days at room temperature or for a shorter time at a slightly higher temperature, will again exhibit a yield point, but at a higher level than previously observed. The time and temperature involved for the return of the yield point is related to the diffusion rate of the nitrogen atoms and is explained as follows. A steel which has been plastically deformed beyond its yield point contains a great number of dislocations which are no longer surrounded by atmospheres of nitrogen. The nitrogen diffuses slowly at room temperature and more rapidly at slightly elevated temperatures and the dislocations again accumulate atmospheres of nitrogen by diffusion. The steel is then in its original state except that the dislocations are now interacting due to plastic deformation, and strengthening has occurred. Therefore, a yield point can again be observed, but at a higher critical stress level.

Cottrell's theory has been extended to include the strain aging peak which is frequently observed for plain carbon steels. As the test temperatures increased for tensile tests, the ultimate tensile strength increases to a maximum at a temperature of about 400^{o} F. Above this temperature, the tensile strength again decreases. Tensile tests which are conducted slightly below the temperature for the maximum ultimate tensile strength exhibit a serrated stress-strain curve. At this temperature, plastic deformation and strain aging occur at approximately the same rate. The serrated stress-strain curve is a result of alternate cycles of yielding and strain aging which occur progressively at higher and higher stresses due to the plastic deformation which has occurred. At temperatures above the strain aging peak, no serrations in the stress-strain curve are noted. Therefore, it has been proposed that, at the strain aging peak, the atmospheres of nitrogen are reformed at the same rate that dislocations are able to escape from an existing atmosphere. A dislocation which has attained sufficient energy to break away from its atmosphere moves slower and slower as deformation proceeds and gathers another atmosphere of nitrogen atoms until it is again trapped by a combination of its interaction with other dislocations and the nitrogen atmosphere which it has collected.

Effect of Strain Aging on Creep Phenomena

At slightly elevated temperatures and stresses at which creep becomes an important phenomenon, the effect of interstitial elements in solid solution is slightly more complex. The effect of the interstitial elements can be best explained by dividing the creep region roughly into two temperature ranges, a low temperature range and a high temperature range. At low temperatures, the dislocations are surrounded by atmospheres of nitrogen, but at these temperatures a lower energy is necessary for the movement of dislocations and many dislocations have sufficient energy to move. At low stress levels, the rate of deformation is slow enough so that deformation can occur by movements of slow dislocations. These dislocations retain their atmospheres of nitrogen which diffuse with the dislocation at a fairly slow rate.

As the stress level is increased, more and more dislocations have sufficient energy to break away from the atmospheres of nitrogen and become active and move more rapidly through the lattice. These "fast" dislocations eventually slow down due to interaction with other dislocations and again collect an atmosphere of nitrogen atoms. However, at rapid strain rates, little effect would be expected since a majority of the deformation would take place by the movement of fast dislocations.

At more elevated temperatures, the picture is complicated by recovery which occurs during the creep tests; however, the relationship between slow and fast dislocations and the stress level should still exist. Due to the increase in temperature, the rate of movement of the slow dislocations is much more rapid. Interacting dislocations can be rendered ineffective by recovery at higher temperatures so that an additional condition is necessary to increase the effect of the interstitial elements. High temperature creep phenomena require an additional element which either causes precipitation of a second phase in minor quantities or creates the potential for precipitation of the interstitial element. Elements such as silicon or aluminum, which have a definite thermodynamic preference for the nitrogen atoms, serve in this capacity. Thus, a dislocation collects an atmosphere not only of nitrogen but of aluminum or silicon and must move at a slower rate, roughly dependent on the diffusion rate of the nitride forming element. The dislocations are further hindered by the small precipitates in the lattice. Additional energy is necessary for recovery due to the other odd sized elements in solution so that interactions between dislocations are effective at the higher temperatures.

There is good experimental evidence to show that strain aging at room temperature and the effect of strain aging for tensile tests at slightly elevated temperatures is directly related to nitrogen in solid solution. Previous investigations have shown that the effect of deoxidation and heat-treatment on phenomena normally connected with strain aging are directly related to the effect of the heat-treatment on the dissolved nitrogen (31). There remains, however, the problem of checking the validity of the strain aging mechanism at the temperatures and stresses involved in the present investigation in order to logically explain the relationship between the dissolved nitrogen and creep rate.

III

EXPERIMENTAL DESIGN, MATERIALS AND PROCEDURE

Experimental Design

It has been proposed that there is a correlation between the creep strength of plain carbon steel and the amount of nitrogen in solid solution in the steel. To show that this correlation exists, a group of commercially and specially produced steels representing various deoxidation practices were obtained and the dissolved nitrogen and the creep rates were determined for these materials.

The basic experimental design evolves into four groups of tests with the following objectives:

1. To show that the creep strength of commercially prepared plain carbon steels varies with deoxidation and heat-treatment as a result of the amount of nitrogen retained in solid solution by these treatments.

2. To show that the effect of deoxidation and heat-treatment on the creep strength is not significant for steels produced with low nitrogen contents.

3. To examine the previously proposed mechanisms for the effect of deoxidation on the creep strength of steel in light of the correlation between the nitrogen and the creep strength and accept or discard these mechanisms on the basis of critically designed experiments.

4. To propose and test a mechanism which will explain the relations between nitrogen and creep strength.

With these objectives in mind, a group of commercial steels which represented rimmed, silicon killed, silicon-aluminum killed, and aluminum killed deoxidation practices, were assembled for testing. The steels were austenitized at 1650° F. and 2150° F. The higher temperature was chosen in order to dissolve the aluminum nitride for the aluminum deoxidized steels. The steels were then furnace cooled and air cooled to vary the amount of nitrogen retained in solid solution at room temperature.

A group of steels, which contained low nitrogen, were prepared by vacuum melting or vacuum extraction. These materials were tested to show that steels, which contained low nitrogen, would have low creep strength regardless of deoxidation practice or heat-treatment.

The commercial materials were subjected to several other processes to investigate the effects of these processes on the creep strength. A silicon and an aluminum killed steel were tested in the as-rolled condition, and the aluminum killed steel was also tested in the stress relieved condition. Two samples of a silicon-aluminum killed steel were rolled from 1750° F. and 2150° F. respectively in order to obtain materials in the as-rolled condition which contained high and low dissolved nitrogen. In addition, a silicon and an aluminum killed steel were subjected to a spheroidizing treatment in order to determine whether the effect of spheroidization on the creep strength was related to the dissolved nitrogen.

Creep tests were run for all these materials at 850° F. and 15,000 psi. The total and insoluble nitrogen were determined for the materials in order to obtain a value for the dissolved nitrogen by difference. Additional creep tests and high temperature tensile tests were conducted on some of the materials to better evaluate the mechanism for the effect of nitrogen on the creep strength.

Both the materials and testing procedures are discussed in greater detail in the following section. Since statistical analysis was used as a tool for evaluating the significance of the correlations developed, the techniques used are also discussed briefly.

Materials

Steels

The effect of deoxidation had been found to be significant at many temperatures for commercial materials. Since the aim of this study was to explain this variation in strength, commercial plain carbon steels were chosen to develop the basic correlation between nitrogen and creep strength. The results of previous investigators in the field of deoxidation effects have shown that the major effects of aluminum deoxidation occur in steels which have been deoxidized with approximately two pounds of aluminum per ton of steel, and that steels deoxidized with one pound of aluminum per ton normally behave as coarse-grained silicon-killed steels. For this reason, a group of commercially prepared steels were assembled with two levels of silicon deoxidation and three levels of aluminum deoxidation as shown in Figure 1.

Fortunately, because of the great amount of research being conducted into the effects of deoxidation, it was possible to assemble such a group of steels for which the deoxidation practice and rolling practice had been carefully recorded. The chemical compositions of these steels are shown in Table I. Steels "A", "D", "E", and "J" were obtained from the Research Laboratories of the United States Steel Corporation through the efforts of R. L. Rickett and bear the same designation as that used in an investigation of the effects of deoxidation and heat-treatment on strain aging (31). Steels "C" and "F" were obtained from the Chemical and Petroleum Panel of The ASTM-ASME Joint Committee on the Effect of Temperature on the Properties of Metals with the help of R. F. Miller of that committee. These steels were in the form of one inch plate in the hot-rolled condition and were among the plate steels tested for Project No. 8 of the Chemical and Petroleum Panel. Steels "C" and "F" were designated CG2 and FG1, respectively, in this previous study (13).

Steel "H" was received in the form of 1-1/4 inch plate from the Allis-Chalmers Manufacturing Company and is a rimmed steel with very high nitrogen content. The details of manufacturing process for this steel are not known; however, the nitrogen content of this steel is as high as that normally found for steel produced by the Bessemer process.

Steel "B" was obtained from the United States Steel Corporation in the form of 2-1/4 inch diameter bar stock. This bar stock was subsequently hot-rolled in a closed pass rolling mill into 7/8 inch square bar stock. The rolling temperature was approximately 2150° F., and at least two reheats were necessary between rolling passes. Following the final reheat, the bar was rolled from 1-1/4 inch square to 7/8 inch square.

Following the basic premise of this study, it was proposed that the primary reason for the reported high creep strength of all steels in the as-rolled condition, regardless of deoxidation, was that these steels were actually rolled above their coarsening temperature and cooled rapidly enough to produce high dissolved nitrogen regardless of deoxidation. In order to test this hypothesis, one bar of steel "B" was heated only to 1750° F. during the final pass in order to produce a steel in the as-rolled condition with low dissolved nitrogen. Since 1750° F. was below the coarsening temperature of the steel, it would be expected that aluminum nitride would be precipitated at the rolling temperature and the steel would contain low dissolved nitrogen in the as-rolled condition.

Several special heats of steel were produced by vacuum melting through the courtesy of the Ford Motor Company and the Engineering Research Institute of the University of Michigan. The chemical analyses of these heats are given in Table II. The heats were melted in vacuum to remove both the nitrogen and the oxygen, and carbon dioxide was introduced into the chamber to reoxidize the steel without increasing the nitrogen content. In this way, it was hoped that the composition of the steels would be comparable to those of the commercially produced heats with the exception of the low nitrogen. For aluminum-killed steels of this type, only minor changes of strength from heat-treatment would be expected if nitrogen were primarily responsible for the change in strength.

Steel 1019 was produced at the Metallurgical Research Laboratories of the Ford Motor Company and had a very low manganese content, evidently due to high loss from vaporization. Heats 1016 and 1018 were produced at the University of Michigan, and similar difficulty with high vaporization loss produced very low manganese in both heats. The difficulties encountered in controlling the composition of relatively volatile elements in vacuum made it evident that it would be very difficult to exactly duplicate the analyses of the commercial heats by vacuum melting. In addition, it was found that some residual aluminum was picked up from either the raw materials or the zirconia crucible. This made the composition even more difficult to control and made it impossible to produce a straight silicon-killed steel in vacuum without considerable experimentation. Therefore, it was decided that the analyses of the vacuum melted heats would be matched by air melted heats produced from similar starting materials. These two heats were melted in a fourteen pound induction furnace at the Allis-Chalmers Research Laboratories, and the chemical analyses are also shown in Table II for comparison. The steels were poured in a cast iron mold with a copper base plate and the assembly held approximately 12 pounds of steel including hot top.

Low nitrogen samples for silicon-killed steel "C" and rimmed steel "A" were produced by vacuum annealing. The samples were held for 100 hours at 2000° F. in a vacuum of less than one micron. The calculation for the removal of nitrogen by diffusion is shown in Calculation 1, in the Appendix, and indicates that all of the nitrogen should be removed by this treatment. The samples were then annealed in vacuum prior to final heat-treatment for testing in order to refine the grain size and minimize the effect of the prior treatment.

The vacuum melted heats were rolled in the closed pass rolling mill with a procedure similar to that used for steel "B". The air melted heats were forged from 2150° F. by a hammer forge into approximately one inch bar stock.

Heat-Treatment

The fine grain heat-treatment temperature of 1650° F. was chosen because it was below the coarsening temperature of those steels which were fine grained as shown by the McQuaid-Ehn grain size. Steels austenitized at this temperature should, therefore, have a variation in dissolved nitrogen depending on deoxidation. The higher austenitizing temperature of 2150° F. was chosen because it was above the coarsening or solution temperature for practically all of the steels tested. Therefore, it would be expected that the dissolved nitrogen in this condition of heat-treatment would vary with both deoxidation and cooling rate. The two temperatures should give the extreme conditions of dissolved nitrogen and creep strength as well as intermediate nitrogen contents depending on cooling rate. The cooling rates were arbitrarily limited to air and furnace cooling since it has been shown by previous studies that the creep rates of the fine grained steels can be changed significantly by these two cooling rates. The bars were heat-treated in sizes no larger than one inch square so that air-cooling was fairly rapid. The cooling rate for furnace cooling varied between approximately 300 degrees per hour to 400 degrees per hour depending on the size of the furnace.

Procedure

Creep Tests

Creep tests were run both at the University of Michigan and at the Allis-Chalmers Research Laboratories and check tests indicate that there is good agreement between the tests run at the two laboratories. The creep tests at the University of Michigan were conducted on several units of slightly differing design, however, both temperature and load were carefully controlled in all cases. The creep rates were measured with the modified Martin's type extensometer with a sensitivity of 4 x 10^{-6} inches per inch. The creep units at the Allis-Chalmers Manufacturing Company are of the overhead beam type with a 15 to 1 beam factor. The furnaces are wound so that each of the five zones in the furnace can be shunted separately in order to obtain good temperature distribution. The creep rates were measured by measuring the relative movement between Knoop hardness indentations in the platinum strip and channel which are fastened to the shoulders of the specimen. These distances are measured by a 100 power microscope with a filiar eyepiece, and the sensitivity of this method was about 2 x 10^{-5} inches per inch. In both laboratories, the temperature of the bar was controlled within two degrees of the control temperature and the temperature of the bottom and top of the bar was within four degrees of the temperature of the center couple.

The majority of the tests were conducted at 850° F. and at a stress of 15,000 psi. A temperature of 850° F. was chosen since many very comprehensive studies had been conducted at this temperature, and it was reasoned that the previously reported values might be of some aid in understanding the effect of varying stress on the creep strength. The stress of 15,000 psi was chosen because it resulted in a reasonable range of creep rates for the large variation in strength anticipated. In some of the first tests, a stress of 10,000 psi was chosen; however, this stress was found to be too low to result in a measurable creep rate for some materials. The stress for these tests was increased to 15,000 psi after the tests had been in progress for approximately 700 hours. This may have resulted in a slight shift in the level of the creep rate, but the results of these tests are still of value. The creep tests were continued for at least 600 hours, and the creep rates were measured for the time interval from 500 to 600 hours. Since some of the tests were continued for times up to 1,000 hours, it was necessary to arbitrarily choose this shorter time in order to permit a comparative evaluation of the various materials. For the majority of the tests, the creep rates so measured were reasonably close to the eventual second-stage creep rate.

High Temperature Tensile Tests

The stress-strain and tensile tests were conducted on a Baldwin-Southwark hydraulic tensile machine equipped with a furnace for elevated temperature tests. An O.S. Peters Model TS-M Dual extensometer modified for elevated temperature use was connected to the stress-strain recorder and automatically produced a stress-strain curve at all temperatures. The speed of deformation was controlled by hand and was kept constant by means of a pace setter which indicated changes in the rate of head movement.

The stress-strain curves were continued slightly beyond the ultimate tensile strength of the material, and the final breaking stress based on the area of the broken section was also recorded. The results of the tensile tests were then used to calculate the true stress and true strain curves from the following equations (32):

$$e_t = \log \frac{A_o}{A} = 2 \log \frac{l}{l_o} \quad \ldots\ldots\ldots\ldots\ldots\ldots \text{III-1}$$

in which:

e_t is the true strain

A and A_o are the true area and original area, respectively

l and l_o are the true length and original length, respectively

From these equations, the true strain and the area at any point can be calculated if the change in length of the sample is known. The true stress at any point can be calculated by dividing the load by the true area of the specimen.

McGregor and others (32, 33) have shown that the plot of true stress and true strain between the ultimate tensile strength and the breaking strength of a specimen is approximately a straight line and, therefore, the complete true stress-true strain diagram can be constructed by drawing a straight line between these two points. A detailed calculation of one true stress-true strain test is included in Calculation 2 in the Appendix. The true stress-true strain method results in a better indication of changes in a material which affect both the strength and ductility. An isostrain diagram, in which the stress for a given strain at the various test temperatures is plotted as one curve, was then constructed for several values of true strain to give a fairly complete picture of the effect of temperature on the stress-strain properties of the steels with various heat-treatments.

Nitrogen and Aluminum Nitride Analyses

The method of analysis for nitrogen and for nitrogen combined as aluminum nitride or other nitrides in the steel has been developed largely through the efforts of H. F. Beeghly (4, 34). In determination of the total nitrogen, digestion in a one to one sulphuric acid solution containing five percent phosphoric acid was found necessary for complete recovery of nitrogen. The solution and separation of the nitrides was accomplished by the methyl acetate-bromine method described by Beeghly. The nitrogen was distilled as ammonia in a micro-Kjeldahl apparatus and collected with 50 cc of distillate in a Nessler tube. The color developed by the Nessler's reagent was measured on a Beckman spectrophotometer at 410 Å wave length with a slit width of 0.15 mm. The Nessler's solution was calibrated with a known solution of ammonium chloride.

Duplicate analyses were conducted on all aluminum nitride analyses for basic correlation. The samples were coded to remove the possibility of operator bias and were randomly arranged so that duplicate samples were not necessarily run on the same day. Since the separations were run in groups of four this served as a cross check between days. The accuracy of the nitrogen determinations was ±0.0005 percent nitrogen.

Statistical Methods

Statistical methods were used to determine the significance of the correlation between the logarithm of creep rate and dissolved nitrogen and also used to determine the limits of accuracy of the analytical method. The Method of Least Square's described by Ezekiel (35) was used to determine the regression equation and the significance of this equation. The accuracy of the aluminum nitride determinations was calculated using the difference between the duplicate samples and the "t" or difference method of statistical analysis (36). The analysis of variance method was used to calculate the significance of heat-treatment on the soluble or metallic aluminum in three aluminum deoxidized steels.

IV

RESULTS

Effect of Deoxidation and Heat-Treatment

Basic Correlation

A group of steels were obtained with the zero and 0.20 percent silicon levels and three levels of aluminum deoxidation as previously mentioned. A graph showing how these materials fit into the basic experimental design and the letter designation for both the deoxidized and rimmed steels is shown in Figure 1. The metallic aluminum and silicon contents of each of the steels are given in this figure. The total nitrogen content of these heats of steel was between 0.004 and 0.005 percent. The two austenitizing temperatures and cooling rates included in the basic correlation experiment, along with the coding used throughout to designate these treatments, are also shown in Figure 1. The austenitic grain size was determined at 1650° F. and 2150° F. for all of the test materials, and these results are listed in Table III. The dissolved nitrogen and creep rate at 500 to 600 hours at 850° F. and 15,000 psi were determined for the four conditions of heat-treatment for all of the commercial heats.

Deoxidized Steels:--The results for the deoxidized steels are listed in Table IV. The logarithm of the creep rate has been plotted against the amount of nitrogen in solid solution in Figure 2. There is a linear decrease in the logarithm of the creep rate with increased nitrogen. The correlation was examined statistically by the method of least squares, and the following relation was determined (Appendix, Calculation 3):

$$\log \overset{\circ}{e} = -2.083 - 593 \times \% \text{ Nitrogen} \quad \ldots\ldots\ldots\ldots \text{IV-1}$$

The corrected correlation coefficient for this equation is 0.923.

The metallic aluminum and insoluble alumina were determined for the four conditions of heat-treatment of steels "B", "E" and "F" which had been heavily deoxidized with aluminum. The results are shown in Table V, and the results of an analysis of variance determination of the significance of the difference between heat-treatment is also shown in this table. There is no significant variation in aluminum or alumina with heat-treatment for these aluminum killed steels.

Rimmed Steels:--Previous authors have shown that the creep behavior of rimmed steels differs from that of deoxidized steels, and the results for the rimmed steels have been analyzed separately. The pertinent details and coding for the rimmed steel experiment are also given in Figure 1. Rimmed steels with two levels of nitrogen were obtained from commercial practice and are designated as steels "A" and "H". An additional sample of steel "A" was heated in vacuum at 2000° F. for approximately 100 hours to remove the nitrogen by diffusion. This sample was subsequently normalized twice to minimize the effects of prior treatment.

Since the literature indicates that all of the nitrogen should be soluble at testing temperature in rimmed steels, only total nitrogen was determined for the two commercial rimmed steels and for steel "A" after the vacuum annealing treatment. The nitride nitrogen was determined for the fine air cooled sample of steel "A" after testing at 850° F. and only 0.0004 percent nitrogen was found in this form. The total nitrogen and the results of the creep test for the rimmed materials are listed in Table VI. The logarithm of the creep rates for these tests are plotted against the total nitrogen in Figure 3, and rimmed steels also exhibit a decrease in creep rate with increased nitrogen.

The best straight line for the logarithm of the creep rate versus percent nitrogen was also determined for the rimmed steels with the assumption that the maximum effect occurred at 0.0063 percent nitrogen (Appendix, Calculation 4). This assumption will be verified later. The equation for this relation to 0.0063 percent nitrogen is:

$$\log \dot{e} = -2.175 - 333 \times \%\ \text{nitrogen} \quad \ldots\ldots\ldots\ldots \text{IV-2}$$

The correlation coefficient for this straight line is 0.976. The correlation curve for the deoxidized steels from Figure 2 is shown in Figure 3 for comparison. The variation in creep strength with nitrogen is not as great for the rimmed steels as for the deoxidized steels; however, the curves apparently intersect at zero nitrogen.

Effect of Other Manufacturing Variables

Effect of Rolling

The creep strength of deoxidized steels in the as-rolled condition has previously been reported to be high regardless of deoxidation. It is proposed that the reason for this lack of variation in strength with deoxidation was the high temperature of rolling, which resulted in high dissolved nitrogen, regardless of deoxidation practice. Steels "C" and "F" were tested in the as-rolled condition, and steel "F" was tested after a stress relief of 1150° F. for two hours.

Samples from steel "B" were also tested in the as-rolled condition with rolling temperatures of 1750° F. and 2150° F. Creep tests were started at 10,000 psi at 850° F., and after approximately 700 hours at this stress the bars were retested at 15,000 psi.

The results of the creep tests and analyses for dissolved nitrogen are shown in Table VII for the steels in the as-rolled condition. Stress relieving of steel "F" caused a decrease in the dissolved nitrogen and a corresponding increase in creep rate. A decrease in creep rate with increased active nitrogen was also found for steels in the as-rolled condition. The relationship between the logarithm of the creep rate and the percent dissolved nitrogen for these steels in the as-rolled condition is plotted in Figure 4. The correlation curve for the heat-treated deoxidixed steels is also shown in this figure. The results for steel "B" are displaced from the correlation curve by an amount that is greater than can be explained by scatter. However, these results were obtained after prior testing at 10,000 psi and 850° F. and it is probable that this displacement was caused by the prior testing.

Effect of Spheroidization

The creep strength in low carbon, plain carbon steels was correlated primarily with the dissolved nitrogen and was not significantly related to the microstructure. This led to the speculation that the loss of strength due to spheroidization might also be caused by the precipitation of the nitrogen in the steel. Therefore, the fine grained air cooled condition of the silicon-killed steel "C" and the coarsened and fine grained air cooled conditions for steel "F" were spheroidized by holding for 100 hours at 1250° F. This treatment was sufficient to spheroidize both materials.

The dissolved nitrogen content for the three samples before and after spheroidization are given in Table VIII along with the resulting creep rates. The variation in strength between the spheroidized and as-treated materials is shown in Figure 5. The spheroidization treatment greatly increased the creep rate of the steels which originally contained high dissolved nitrogen. The fine grained condition of the aluminum killed steel exhibited little change in creep rate. Since the nitrogen was already precipitated by the original heat-treatment for the fine grained material, the change in dissolved nitrogen with spheroidization was also very small. The creep rates are plotted against the dissolved nitrogen for both the as heat-treated and spheroidized condition in Figure 6. The correlation curve for the heat-treated deoxidized steels is also given in this figure for comparison. The creep rates for the spheroidized steels are very close to the rate predicted by the active nitrogen in these materials.

Effect of Other Variables

Low Nitrogen Steels

As it became evident that the amount of nitrogen in solid solution could be correlated with the creep strength of plain carbon steels, a question arose. What would be expected from a group of steels which had low nitrogen as a result of vacuum melting or some similar process? It was proposed that silicon-killed steels with low nitrogen should have reduced creep strength due to the removal of the nitrogen. Also, the variation in creep strength with austenitizing temperature for aluminum-killed steels should be greatly reduced or possibly eliminated for vacuum melted steels. The samples were prepared both by vacuum melting and vacuum annealing as previously discussed.

The nitrogen was removed from two samples of steel "C" by annealing in vacuum for 100 hours at 2000° F. As in the case of the vacuum annealed, rimmed steel, a double normalizing treatment was given to minimize the effects of long time at high temperature. The microstructures were of the Widmanstätten type normally expected for an air cooled silicon-killed steel, Figure 7. The resulting creep strength and total nitrogen for the steels are listed in Table IX, and the logarithm of the creep rate is plotted against the total nitrogen in Figure 8. The results for steel "C" in the high nitrogen condition and the correlation curve for the deoxidized steels are also shown in this figure. The creep rate for the vacuum extracted sample of steel "C" is in the range predicted by the nitrogen content.

The vacuum melted steels and the corresponding air melted steels with similar analyses were also tested at 15,000 psi at 850° F. Because of the extreme weakness of these vacuum melted steels, some of the tests ruptured in times as short as 100 to 500 hours, and in these cases the creep rates, Table IX, are the minimum rates observed for the test. Since all of these steels are effectively aluminum killed because of the high residual metallic aluminum, these steels were tested in the fine and coarsened air cooled condition. The dissolved nitrogen and the creep rates for these steels are given in Table IX. Steel 1019 is compared with its equivalent low manganese air melted steel 1379 in Figure 9 for both the coarsened and fine grained air cooled condition. Steels 1018 and 1442 are similarly compared in this figure and represent a higher manganese level.

The creep rates for the vacuum melted samples were high regardless of austenitizing temperature. The creep rates of the fine grained condition of the air melted steels were equally high. However, the coarsened condition for comparable air melted steels exhibited much lower creep rates as a result of the increase in dissolved nitrogen.

Manganese Effect

The results for the vacuum melted steels made it evident that some additional variable was responsible for a change in the level of the creep strength. However, this variable is not directly connected with the deoxidation effect as shown by the lack of variation between creep strength and heat-treatment for the low nitrogen aluminum-bearing steels. The major change in composition for the vacuum melted steels was the low manganese content.

The creep strength for most of the steels had been determined in some condition of heat treatment which yielded a low dissolved nitrogen; therefore, the effect of manganese on the creep strength was checked by plotting the creep rate versus the manganese content for those steels which contained between 0.001 and 0.002 percent dissolved nitrogen, Figure 10. The results indicate that manganese has an important influence by increasing the level of strength of carbon steel.

In order to test the significance of this relation, the correlation between manganese and creep rate for these steels was determined by the least squares method. The details of this calculation are given in Calculation 5 in the Appendix and the results are as follows:

$$\log \dot{e} = -0.772 - 33.8 \times \%\ \text{Manganese} \quad \ldots\ldots\ldots\text{IV-3}$$

The corrected correlation coefficient was 0.901 which is very significant.

Effect of Other Variables on the Basic Correlation Curve

Since there was a correlation between the manganese content and the level of strength for steels at a given nitrogen content, it was thought that possibly some of the variations from the correlation curve could be accounted for by manganese content, deoxidation or heat-treatment variables. The effects of these variables were tested by an analysis of variance of the deviation from the correlation curve for the heat-treated deoxidized steels. These calculations are summarized in Calculations 6 and 7 in the Appendix, and the results are as follows.

The various heat-treatments employed caused no significant variation. There was no significant variation from the curve for any one individual steel or any group of steels. There was, however, an indication that those steels, which were air cooled from either the fine or coarse grained austenite were on the high strength side of the correlation curve, and those which were furnace cooled were on the low strength side. This relationship was not statistically significant.

The as-received hardnesses for the heat-treated deoxidized steels and for the steels used in the other tests are listed in Tables X and XI, respectively. Hardnesses were obtained on the as-treated materials and on the reduced section and shoulder section after testing. The hardness in the reduced section represents the hardness after testing for the strained material and those in the shoulder section represent the unstrained, heated condition. The deviations from the creep rate correlation curve of Figure 2 were tested statistically for possible effects of hardness, Appendix, Calculation 8, and the effect of hardness was not significant.

The lack of variation between steels indicated that manganese was not responsible for the scatter in the correlation curve for the heat-treated deoxidized materials.

The manganese content of these steels varied from 0.42 to 0.82 percent which is within the expected range for commercial plain carbon steels. The effect of manganese determined for steels with 0.005 to 0.82 percent manganese at low active nitrogen levels was significant. Perhaps this paradox for the effect of manganese could be clarified by a study of steels with a wider range of manganese variation at several levels of dissolved nitrogen. It is also possible that cooling rate and hardness influence the creep strength over a wider range of variation at a given nitrogen level.

Mechanism Tests

A group of tests were devised to check the possible mechanisms for the effect of nitrogen on the creep strength. Cross (9) has previously shown that neither grain size nor microstructure could be related to the change in creep strength, and this conclusion is substantiated by the present study. A precipitation strengthening mechanism based on the solution and precipitation of nitrogen with varying deoxidation and heat-treatment should be considered. Cross (9) proposed such a mechanism based on the hypothetical solution and precipitation of "X". It is now obvious that "X" is aluminum nitride. In addition, a strain aging mechanism was also examined since nitrogen is known to be important to strain aging of plain carbon steel.

In order to determine if a precipitation strengthening phenomenon was responsible for the increase in creep strength, the combined nitrogen, after creep testing, was determined for several of the steels tested, Table XII. The combined nitrogen, determined by Beeghly's method for the as-heat-treated material, and the change in combined nitrogen during test are also listed in this table. A slight increase in the amount of aluminum nitride has occurred for the deoxidized steels.

Isostrain curves were determined for samples of steels "C" and "F" which had been air cooled from both 2150° F. and 1650° F. These tests were conducted by the method outlined by MacGregor (32), and the results for the individual steels in the two conditions of heat-treatment are shown for true strains of 0.05, 0.10, 0.50, and 1.00 inches per inch, Figure 11. The results for all four materials have been compiled in Figure 11 for true strains of 0.05 and 0.5 inches per inch. For the materials which contained high dissolved nitrogen there is an increase in strength with increasing temperature which reaches a maximum at 400° F. This behavior gives rise to a "strain aging" peak at about 400° F. Steel "F" in the fine grained air cooled condition exhibited no "strain aging" peak.

As previously mentioned, steels tested at 1000° F. at very low stresses showed creep rates which were alternately high and low as the tests progressed. These tests were conducted for the stress relieved condition of steels "F" and "C" for times up to 8,000 hours. The resulting creep rates are plotted against time for these materials in Figure 12. Steel "F" at two stress levels showed a very low initial creep rate and a subsequent increase in creep rate after about 1,000 to 1,500 hours of testing. The creep rates reached a maximum and again decreased. Steel "F" at 2,000 psi went through another maximum at about 5,500 hours. Steel "C", which was a silicon-killed material, showed a normal creep rate-time curve out to about 2,500 hours after which a very rapid increase in creep rate was experienced. The creep rate for this test reached a maximum at about 4,000 hours and again decreased for longer times. Although the tests were not run beyond 8,000 hours, steel "C" apparently would have gone through a series of alternately high and low creep rates and eventually reach a lower creep rate, as did the other two samples.

A series of tests were run at constant temperature with varying stress, Figure 13, and varying temperature with constant stress, Figure 14, in order to better understand the effect of stress and temperature on the mechanism involved. Steel "C", air cooled from 1650° F., and two samples of steel "F", air and furnace cooled from 2150° F. were tested at 15,000 psi with varying temperature. The resulting creep curves are shown in Figure 14. These tests were conducted at a constant stress in an attempt to determine whether there was a difference in activation energy for steels with varying dissolved nitrogen. At 900° F., a phenomenon similar to that observed at 1000° F. was found. The creep rate at the start of the 900° F. test was reasonable for the steel at that temperature; however, the creep rate increased after several hundred hours of testing had taken place. This phenomenon was observed, however, only for steels "FCA" and "CFA" which originally had high dissolved nitrogen. Steel "FCF", which had low dissolved nitrogen, showed a normal creep curve at 900° F. The resulting creep curves were not entirely satisfactory for an accurate determination of the activation energy. The results do indicate that the oscillating creep rate behavior observed at 1000° F. does not occur for steels with low dissolved nitrogen. A creep curve for steel "F" in the coarsened air cooled condition was obtained with varying stress at 850° F. and is shown in Figure 13. This steel was tested in a stress range of from 17,000 to 22,500 psi. As the stress was increased from 20,000 psi to 21,875 psi, little change in creep rate was observed. However, at 22,250 psi, the rate increased very rapidly. The reduction of stress to 20,375 psi resulted in a large change in creep rate to the range of that originally observed. An additional decrease in stress to 18,625 psi caused no additional change in creep rate; however, the final stress of 17,000 psi caused the creep rate to decrease further. These tests indicate that there is a critical stress above which the creep rate increases very rapidly.

Additional creep data were obtained from the literature (3, 8, 9, 10, 13, 14) for steels which should contain high and low dissolved nitrogen, and the creep rate-stress curve is shown in Figure 15 for 850° F. and 1000° F. At both temperatures, a maximum effect is apparent for the difference in strength between low and high dissolved nitrogen. At very high creep rates, little or no effect is observed for varying nitrogen, and at low creep rates the curves at 850° F. again seem to converge. These results are in good agreement with the rupture tests at 1000° F. for these materials, which showed no difference in rupture strength between steels with low and high dissolved nitrogen at high stresses at 1000° F. (13).

The creep curve at 850° F. in Figure 15 for the coarsened or high nitrogen condition shows a change in slope at about 22,000 psi with stresses above this value causing a much larger increase in creep rate. This confirms the observations for the behavior of the test with varying stress at 850° F. There apparently is a critical stress at each test temperature above which nitrogen is less effective in interfering with the creep process.

V

DISCUSSION OF THE RESULTS

Relation of Dissolved Nitrogen and Creep Strength

Heat-Treated Deoxidized Steels

A correlation was found between the creep strength of plain carbon steel and the dissolved active nitrogen in the steel for varying deoxidation practices and heat-treatments. An increase in the active nitrogen resulted in a large decrease in creep rate for the heat-treated deoxidized steel as shown in Figure 2. The correlation was examined statistically and the high correlation coefficient is valid proof that the correlation exists. This relation was developed for commercially manufactured steels, and the extremes in deoxidation practice and significant variations in heat-treatment were included in the test program. The large variation in creep rate of the deoxidized steels was related to the nitrogen retained in solid solution by prior processing to a degree which far overshadowed any other differences which existed between the steels tested.

The microstructures of the steels tested included the extremes in ferritic grain size and carbide distribution for mild plain carbon steels. The lack of dependence of creep rate on microstructure is perhaps more markedly shown by a series of microstructures for steels "C" and "F", Figure 16. The microstructures of the coarsened air cooled conditions of the two steels are very similar, and the creep rates in this condition are also of the same order of magnitude. The microstructure of these two steels in the coarsened furnace cooled condition are also similar. Both steels have been cooled from the coarsened austenite. However, the creep rates of these two steels vary by a factor of more than 30. The microstructure of the two steels in the fine, air cooled and fine, furnace cooled conditions show no significant differences in carbide distribution or ferritic grain size between the two steels. However, the creep rates again vary significantly between the aluminum and silicon killed steels, Figure 17.

The microstructures in Figure 18 show that varying carbon content and its influence on the microstructure does not cause a significant variation in the level of creep strength. For example, steel "D" contains 0.10 percent carbon, and the microstructure consists largely of ferrite. The carbides in this material are distributed uniformly throughout the microstructure in both the fine and coarse air cooled conditions. The maximum creep strength of steel "D" did not vary significantly from that of steel "C" which contained a higher percentage of well distributed carbides.

The complete lack of correlation of creep rate with microstructure grain size or carbide distribution confirms the results obtained by Cross (9). The good correlation of the creep rate with the dissolved nitrogen strongly indicates that the important factor involved in the variation of creep strength of steels with deoxidation and heat-treatment is the nitrogen contained in solid solution as a result of these treatments.

Effect of Other Processing Variables

Rolling and Stress Relieving:--Steels "C" and "F" in the as-rolled condition contained high dissolved nitrogen and had high creep strength. Stress relieving steel "F" caused precipitation of some of the nitrogen and greatly reduced the creep strength. The creep rates for all three materials were in the range predicted by the dissolved nitrogen and the correlation curve for the heat-treated deoxidized steels, Figure 4. The creep rate for steel "B" rolled at 1650° F. and 2150° F. also varied with the dissolved nitrogen resulting from these two treatments, Figure 4; however, the creep rates for this steel have been displaced from the correlation curve because of prior testing.

The microstructures of the steels in the as-rolled condition are given in Figure 19. For steels "C" and "F" there is no apparent variation in microstructure, either between deoxidation or as a result of the stress relieving operation for these steels. The structure of the steels consists of a moderately fine ferritic structure with well distributed carbides tending somewhat toward a Widmanstätten type structure. Stress relieving of steel "F" resulted in no apparent change in the pearlite or in the ferrite matrix.

A similar situation exists for the low and high temperature rolling treatments for steel "B". The microstructures of steel "B" in these two conditions, shown in Figure 19, are very similar and are typical of a low carbon aluminum killed steel in the fine grained air cooled condition. There is no difference in microstructure or grain size between the two conditions of rolling although the creep rates varied significantly.

Spheroidization:--Spheroidization did not significantly change the creep strength of the fine grained air cooled aluminum killed steels which originally contained low dissolved nitrogen. However, spheroidization significantly reduced the strength of both aluminum and silicon killed steels with high dissolved nitrogen, as shown in Figure 5, because the spheroidization also caused precipitation of the nitrogen.

The microstructures for the three spheroidized steels are given in Figure 20. The coarsened condition of both steel "F" and steel "C" still show indications of the Widmanstatten structure, typical for this condition. On the other hand, the fine grained air cooled condition of steel "F" shows a marked change in the carbide structure. The grain size of the fine air cooled condition is somewhat finer than that shown in the microstructure of the other two spheroidized steels. However, there is little difference between the creep rates of these three steels in the spheroidized condition. It is significant that the gross changes in carbide distribution caused by spheroidization did not result in a significant deviation from the correlation curve for heat-treated deoxidized steels as shown in Figure 6.

Spheroidization of the fine grained aluminum killed steel progressed more rapidly and would have caused a greater change in the strength for the steel in the fine grained condition if microstructure were the important factor. However, since there was very little change in the amount of dissolved nitrogen, the creep strength did not change significantly. On the other hand, the Widmanstätten structures of steel "C" and steel "F" in the coarsened air cooled conditions are more resistant to spheroidization. However, a major change in the amount of dissolved nitrogen occurred during spheroidization for these materials, and the creep strength in the spheroidized condition was reduced by an amount predicted by the correlation curve.

The effect of hot rolling, stress relieving and spheroidization on the creep strength is clearly related to the dissolved nitrogen in the steel. The commercial plain carbon steels in the as-rolled condition contained high dissolved nitrogen because of the high temperature of rolling and therefore possessed high creep strength regardless of deoxidation practice. Any variation in rolling practice or a subsequent stress relieving treatment, which reduced the nitrogen in solution, caused a simultaneous loss of creep strength. The creep strength of the high dissolved nitrogen conditions of both silicon and aluminum killed steels was reduced by the precipitation of aluminum or silicon nitride during the spheroidization treatment. It would therefore seem likely that any prior treatment which causes the precipitation of nitrogen in an inactive form could be expected to reduce the creep strength.

Low Nitrogen Steels

The results for the creep tests for the vacuum melted and vacuum annealed steels are further proof that nitrogen is the main element involved in the deoxidation effect on the creep strength. For example, the removal of the nitrogen by vacuum extraction from the silicon killed steel "C" resulted in a higher creep rate for both conditions of heat-treatment. This reduction in creep strength was related by the correlation curve to the decrease in dissolved or active nitrogen as shown in Figure 8. A similar reduction in strength resulted for the rimmed steel "A" due to the removal of nitrogen.

The vacuum extracted sample of steel "C" had a coarse Widmanstätten structure as shown in Figure 7, and the austenitic grain size of this material was large. The two conditions are generally indicative of high creep strength, but the lower nitrogen content for these samples resulted in a reduction in creep strength.

The removal of nitrogen by vacuum melting for the strongly deoxidized aluminum killed steels caused a very significant change in the effect of heat-treatment on the creep rate. The creep rates for steel 1019, which had only 0.0017 percent nitrogen, in the coarsened and fine grained air cooled conditions were very similar, Figure 9. An air melted steel of similar composition, but with 0.0094 percent nitrogen showed a change in creep rate of about three cycles on a logarithmic scale between the fine and coarse grained, air cooled condition. Similar results are seen for the comparison of steels 1018 and 1442.

These results also indicate that the method of removal of the nitrogen is not important. The creep rates are practically identical for both conditions of steel 1019 with low total nitrogen and for the fine grained condition of steel 1379 with low dissolved nitrogen. The nitrogen in steel 1379 had been removed by precipitation of aluminum nitride due to the low austenitizing temperature but this effectively reduced the strength to that of the vacuum melted steels. A comparison of steels 1018 and 1442 leads to a similar conclusion, although the level of strength for these heats differs from that of steels

1019 and 1379. Steels 1018 and 1442 contained about 0.30 percent manganese and the level of strength would be expected to be higher because of the significant increase in the level of strength due to manganese. A plot of the creep strength versus active nitrogen for the vacuum melted and vacuum extracted steels is shown in Figure 21 along with the results for the comparable air melted steels. It was assumed that the manganese affects the level of strength uniformly over the entire range of nitrogen, and parallel lines have been drawn for the different manganese levels. A dotted line has also been drawn to include the high active nitrogen condition of steel 1379, and a break in the curve occurs approximately at 0.006 percent nitrogen. The microstructure of steel 1019 is shown in Figure 22 in the fine grained air cooled condition and is similar to other steels of this carbon content.

The relation of nitrogen to creep strength explains some of the results previously reported for silicon killed steels. The creep strength of British steel "E", tested by Cross (9), was abnormally low, in spite of the fact that it had been deoxidized only with silicon. Further checks on the chemical analysis showed that the nitrogen content of the steel was 0.002 percent, which is abnormally low for this type material (10). However, the low nitrogen could be expected to result in lower creep strength for this material. The reported results of reference 10 for the 0.5 percent silicon steels can also be explained on the basis of change in the amount of dissolved nitrogen. Beeghly (34) has shown that, at about 0.5 percent silicon, silicon nitride is precipitated after austenitizing from temperatures just above the critical region. The precipitation of nitrogen as silicon nitride would remove the nitrogen from solid solution and would result in low creep strength as was experienced for these steels.

Rimmed Steels

The relation between nitrogen and creep rate for the rimmed steels is significant in several respects. The microstructures of steels "A" and "H" in the coarsened air cooled and coarsened furnace cooled conditions are shown in Figure 23. There is a significant variation between the ferritic grain size and cooling rate which is expected for ferritic materials. However, there is no significant variation between the creep strengths for the two conditions of heat-treatment. There is a difference between the creep rates of the two steels and this difference is related to the total nitrogen in the steels.

The intercept of the correlation curve for rimmed steel at zero percent nitrogen is, for all practical purposes, the same as the zero intercept for the deoxidized materials. This fact indicates that, in the complete absence of nitrogen, there is no significant difference in the creep strength of rimmed and deoxidized steels at 850° F.

The variation in creep strength for rimmed steels is also a result of the dissolved nitrogen, although the strengthening effect is less pronounced than for deoxidized steels. Results in the literature (6) indicate that, at temperatures of about 600° F., the rimmed steels are as strong as the silicon deoxidized steel, and therefore the relationship for rimmed steels at 850° F. cannot be extended to all temperature ranges. As a matter of fact, it would be expected that the variation between creep strength and nitrogen for rimmed and deoxidized steels at 600° F. would be very similar. At temperatures higher than 850° F., it would be expected that nitrogen would have a less pronounced effect on the creep strength of rimmed steels.

The nitrogen correlation explains the test results for rimmed steels in reference 8 and 9. Cross found that the core material had greater creep strength than that of the rim material for rimmed steels. Results in the literature indicate that the core material has a higher nitrogen level than the rimmed material (37), and this difference is statistically significant, Appendix, Calculation 9. Therefore, it would be expected that, for rimmed steels in general, the higher nitrogen in the core material would result in a higher creep strength for this material.

Causes of Scatter

The scatter around the correlation curve in Figure 2 is about one percent of the total variation in creep rate with active nitrogen over the range of nitrogen contents of the steels tested. The effect of manganese, deoxidation practice, heat-treatment, hardness and microstructure on the scatter were examined for the commercial material. None of these variables had a definite influence on the level of strength for the commercial materials exclusive of the effect on the dissolved nitrogen in the steel. This is not surprising however if it is considered that the normal variation in measurements of creep rate and nitrogen contents could easily represent a sizable part of the total scatter. Manganese had a definite effect on the level of creep strength at low nitrogen contents, Figure 10. From Figure 21, it appears as if increased manganese in the range of 0.0 to 0.40 percent causes a decrease in creep rate at all levels of nitrogen. No definite conclusions can be given for such sparce data and these trends have only been indicated here. These results do show that after the importance of the effect of nitrogen is understood it is possible to better determine the effects of other alloying elements on the high temperature strength.

Discussion of the Mechanism

The large change in creep strength of plain carbon steels with deoxidation and heat-treatment is directly related to the nitrogen in solid solution in the steel after processing. No acceptable mechanism can be based on changes in carbide structures or grain size because of the lack of consistent correlation of creep strength with these two variables.

The solution and precipitation of aluminum oxide with austenitizing temperature and cooling rate does not occur as shown by the lack of significant variation between heat-treatments for the aluminum oxide, Table V. There was no real change in either alumina or aluminum with heat-treatment for the three steels tested. The solution behavior of nitrides with deoxidation, austenitizing temperature and cooling rate is similar to that which Cross (9) proposed for the oxides; therefore, the lack of variation of oxides does not exclude a precipitation mechanism.

The important fact to be explained is how a minute increase in the amount of nitrogen in solution at the start of creep testing can cause a large increase in creep strength. There are two mechanisms which could possibly explain this relationship. The precipitation of finely divided submicroscopic particles proposed by Cross must be considered. A mechanism for the effect of strain aging on materials under creep conditions has been outlined by Cottrell and should also be considered. The precipitation mechanism proposed by Cross has been previously discussed in Section II. A brief summary of Cottrell's theory for strain aging phenomena is also included in Section II.

A mechanism involving the precipitation of coherent submicroscopic particles and a mechanism based on Cottrell's strain aging theories are at least in partial agreement with the results. Both mechanisms require the solution of nitrogen to explain the effect of active nitrogen on the creep strength. However, the tests of these two mechanisms indicate that neither can explain all of the results.

The isostrain tensile test results in Figure 11 indicate that steels with high dissolved nitrogen undergo an increase in strength with temperature up to 400° F. Over this temperature range, steels with low dissolved nitrogen do not exhibit increased tensile strength. The difference in strength between the two conditions of nitrogen reaches a maximum at about 400° F. and above this temperature the strength of the two materials gradually approaches a common value. The increase in strength for the high nitrogen materials is not associated with a change in room temperature hardness. Bars of steel "C", which contained high dissolved nitrogen, were heated to 400° F. for one hour and showed no change in hardness at room temperature. The hardnesses of the shoulder sections of the creep bars showed a negligible increase or decrease in hardness after testing and this minor change in hardness bore no relationship to the creep rates of the materials.

These results cannot be reconciled with a precipitation mechanism. A precipitation mechanism would be expected to cause an increase in hardness for temperature conditions which resulted in increased strength. This is not the case in any of the phenomena involving dissolved nitrogen. The maximum difference in strength between high and low nitrogen steels occurred at about 400° F. for the isostrain tensile results. An apparent maximum effect of nitrogen on the strength occurs at much higher temperatures for tests with lower strain rates, Figure 15. For example, nitrogen has no apparent influence on the strength of steels at 1000° F. for stresses above 10,000 psi, but causes a major change in creep rate in the range of 4,000 psi. Similarly, the creep rate curves at 850° F. show the largest effect for differences in nitrogen at about 22,000 psi, Figure 15.

These observations clearly indicate that the mechanism is a dynamic one involving plastic deformation rather than a simple precipitation reaction. Isostrain peaks observed by Glenn (33) for various alloy additions in steel also occurred at temperatures below the temperature range in which these elements still have an important influence on the creep properties.

Beeghly's method of analysis showed an increase in the amount of nitride nitrogen in the steels after creep testing, Table XII. These results indicate that the amount of active nitrogen has decreased during the test even at 850° F. However, if the actual active nitrogen in the steel had decreased, then an increase in creep rate would be expected. This was not the case.

The precipitation of all of the nitrogen during test would be expected if precipitation of the nitrogen were responsible for the change in strength. The correlation exists between the nitrogen in solution in the steel prior to testing and the creep strength. In order to explain this correlation on the basis of precipitation, all of the nitrogen should have precipitated in a form which interfered with creep. The results in Table XII show that only part of the nitrogen has precipitated and the amount precipitated has no direct relation to the strength.

However, these same results pose a problem in accepting a strain aging mechanism because the nitrogen must be free to move to dislocations in order to continually strengthen the material. No increase in creep rate was observed during any of the creep tests at 850° F, although the results of Table XII indicate a decrease in dissolved nitrogen. The creep tests at 1000° F. in Figure 12 showed a rapid increase in rate early in the test; however, the creep rates of these steels decreased to the original rate for longer times.

It is possible that Beeghly's method of analysis does have some limitations in that nitrogen or nitrides, which are still active in terms of interfering with the creep process, are collected by Beeghly's separation. Internal friction studies indicate that the nitrogen in iron alloyed with manganese, chromium, molybdenum and others form a type of pre-precipitated nitride in solid solution (38, 39). It is claimed that these compound groupings interfere with the complete precipitation of nitrides as measured by changes in internal friction (38). It is possible that a pre-precipitated phase, which is still in a state which interferes with the creep process, was detected by Beeghly's method of analysis. This phase could be either nitrides of aluminum or silicon. If the existence of these pre-precipitated phases could be confirmed for tested creep bars, then a modified strain aging mechanism could be accepted without reservation.

Further study of the mechanism was based on the assumption that some modification of Cottrell's strain aging mechanism was responsible for the decrease in creep rate with increased dissolved nitrogen. It was further assumed that the increased strength was associated with an increased activation energy for the movement of "trapped" dislocations.

The activation energy was calculated by Dorn's method (40) from the tests at a constant stress and varying temperature, and also from the maximum and minimum nitrogen for the deoxidized steels and the special air melted steels. Additional results were obtained from the literature (7, 40). A summary of the calculated activation energies and those obtained from the literature are given in Table XIII.

Cottrell's strain aging mechanism was derived to explain the strengthening behavior caused by interstitial solution elements. If we examine the results in light of this mechanism, certain observations can be explained. Cottrell assumed that the nitrogen atmosphere increased the energy for movement of dislocations.

For the calculations for constant temperature and variable nitrogen, there is a difference in activation energy associated with a difference in nitrogen for both the rimmed and deoxidized steels. This increment in activation energy is in the range of the activation energy for the diffusion of nitrogen in steel. The results for the tests at constant stress and variable temperature for low and high nitrogen steels also show an increase in activation energy with increased nitrogen. The creep curves for these calculations, shown in Figure 14, show unusual behavior at 900° F.; therefore, the activation energy calculations in this case are not reliable. Dorn (40) calculated the activation energy from rupture test results for plain carbon and low alloy steels and found that the energy varied from 90,000 to 105,000 al./mole. The indications of the activation energy data are that increased nitrogen in steel results in an increase in the activation energy for the creep process. Since the activation energies shown in Table XIII were not accurately determined, the actual values are not reliable enough to permit any conclusions concerning the magnitude of the change in activation energy with nitrogen.

From the results for the rimmed steels shown in Figure 3, and for the very low manganese air melted steels in Figure 21, it appears that additional dissolved nitrogen above about 0.006 percent did not cause an additional decrease in creep rate. A strain aging mechanism would predict that additional nitrogen in excess of the amount necessary to form atmospheres around each dislocation should not cause further strengthening. To test this hypothesis, the number of nitrogen atoms for a given surface one atom layer thick was calculated for steel containing 0.0063 percent nitrogen, Appendix, Calculation 10. There are 2 x 10^{11} atoms of nitrogen per square centimeter at the 0.0063 percent nitrogen level. Estimates of the number of dislocations in the same area vary from 10^8

for annealed materials to 10^{12} for severely cold worked materials (41).

The number of atoms of nitrogen for the formation of an "atmosphere" is not known, but assuming an average dislocation length of about 500 Å about 200 atoms would be necessary for each plane through the dislocation. This gives a value of 1×10^9 atmospheres for about 1×10^8 dislocations. The agreement between these two values is reasonable. No stronger conclusion is possible. Both the rimmed steels and the air melted steels show a maximum effective nitrogen, and this is further support for a Cottrell type mechanism.

The weight of evidence from the results of the mechanism tests indicated that a strain aging mechanism is responsible for the change in strength. There was no evidence of an increase in room temperature hardness for steels heated to 400° F. (where the isostrain "peaks" were observed) or for tested creep bars. There was no consistent relation between the amount of nitrogen precipitated during test and the creep strength of the materials.

The increase in strength with increased nitrogen is controlled by stress rather than strain rate. The dissolved nitrogen caused the greatest increase in tensile strength at 400° F. for the strain rate of the tensile tests. At 850° F. and 1000° F. the effect of nitrogen on the creep strength is reduced at high stress levels and occurs primarily at slow strain rates. If strain rate were the controlling factor, then it would be expected that nitrogen would be effective only at a more rapid strain rate at higher temperatures since the rate of diffusion of nitrogen increases with temperature. This was not the case. If stress were the controlling factor then the stress for activation of "trapped" dislocations could be expected to decrease with temperature since the increased thermal energy of the atoms would supply part of the necessary activation energy. This is in agreement with the observations from the effect of nitrogen on the isostrain tests above 400° F. and the lower "critical" stresses for the effect of nitrogen at 850° F. and 1000° F.

There is every indication that the mechanism involved is a dynamic phenomenon involving plastic deformation as well as the solution of nitrogen. However, Beeghly's method of analysis indicated that precipitation of part of the nitrogen occurred during testing at 850° F. without the increase in creep rate which presumably should occur when an increase in precipitated nitrogen is detected. At 1000° F., a reduction in strength occurred after several hundred hours, but the creep rate eventually decreased again and, in one case, went through several cycles of high and low creep rate. These results would not be expected if the nitrogen were precipitated in an inactive form. There is the possibility that, as deformation proceeds during the creep test, groups of interacting dislocations with their atmospheres of nitrogen are so closely bonded with iron and the minor alloys that they effectively form a pre-precipitate phase during testing which is detected by Beeghly's method. If such groupings of nitrogen and other elements in the steel were closely bound to the dislocations and, therefore, still active in preventing further deformation, Cottrell's mechanism would be acceptable.

On the basis of these tests, Cottrell's mechanism can not be accepted without reservation. However, the approach for further fruitful research into this problem is apparent. The mechanism involved apparently results in a strengthening effect for nitrogen below a critical stress level and the stress decreases with temperature. A study could be made of the precipitates obtained by Beeghly's method by X-ray or electron diffraction studies and electron microscope studies to determine whether the precipitates, which form during testing, are aluminum or silicon nitrides or some pre-precipitation phase. For the present, it can be concluded that the mechanism involved is stress sensitive, that is, probably a dynamic rather than a static strengthening phenomenon. The true mechanism follows very closely with the predictions of Cottrell's theory in that its effect is detected only under conditions which involve plastic deformation.

VI

SUMMARY AND CONCLUSIONS

The correlation between the creep strength of plain carbon steels and the nitrogen in solid solution in the steels has been studied in order to explain the fundamentals involved in the variation of creep strength with deoxidation, heat-treatment and other prior processing variables which affect the creep strength at elevated temperatures. Steels from commercial practice and specially prepared vacuum melted and air melted steels were studied with the following results.

1. For deoxidized steels, the effect of deoxidation and heat-treatment on the creep strength of plain carbon steels can be directly related to the nitrogen in solid solution in these steels as a result of these variables. At 850° F. and 15,000 psi there is a linear decrease in the logarithm of the creep rate with an increase in dissolved nitrogen in the steel which is given by the following equation:

   $\log \dot{e} = -2.083 - 593 \times \%$ dissolved nitrogen

2. The total nitrogen and creep strength are similarly correlated for rimmed steels by the following equation:

   $\log \dot{e} = -2.175 - 333 \times \%$ nitrogen

   The change in creep strength is less drastic for rimmed steels, but the creep rate for zero percent nitrogen is about the same as that of deoxidized steels.

3. The results of other metallurgical processes on the creep strength of steel are as follows: Both silicon and aluminum killed steels in the hot rolled condition possess high creep strength because the dissolved nitrogen is high. Any subsequent treatment which causes the precipitation of aluminum nitride and lowers the dissolved nitrogen, substantially reduces the creep strength. Spheroidization causes drastic changes in the creep strength of silicon and coarsened aluminum killed steels due to the precipitation of nitrogen but causes little change in the creep strength of the fine grained aluminum killed steels in which nitrogen is already precipitated.

   In all cases the creep strength, which resulted from a change in processing history, was related to the resulting dissolved nitrogen.

4. For steels with low nitrogen obtained by vacuum melting or vacuum extraction, the creep strength is low regardless of deoxidation or heat treatment. The level of creep strength for steels with low nitrogen is the same as that of similar steels in which the nitrogen was removed by precipitation of aluminum nitride. Therefore, steels with low dissolved nitrogen have low creep strength regardless of the method of nitrogen removal.

5. Deoxidation, heat treatment, carbide distribution, and grain size caused no deviation from the correlation curve for the commercial deoxidized steels which could be related to these factors. The manganese content and the hardness may cause minor variations from this curve; however, for air and furnace cooled mild steels in the range of commercial compositions only the effect of dissolved nitrogen was found to be significant. Manganese over a wider range of 0.00 to 0.82 percent manganese caused a variation in the level of the creep strength for steels with low nitrogen. The strong relation between creep strength and dissolved nitrogen still existed at all manganese levels.

The creep strength of steel is related to the dissolved nitrogen in the steel prior to creep testing. Silicon killed steels generally have high strength because silicon nitride does not precipitate with normal heat treatment. Spheroidization or any other process which caused precipitation of silicon nitride would decrease the strength of silicon killed steels. The nitrogen in aluminum killed steels is precipitated as aluminum nitride for most conditions of heat treatment and these steels have poor creep strength. Heating an aluminum killed steel above the coarsening temperature dissolves the aluminum nitride and fairly rapid cooling retains the nitrogen in solid solution. The creep strength in the high nitrogen condition is high. The nitrogen in rimmed steels is in solid solution regardless of heat treatment. At 600° F. the creep strength of rimmed steels is as high as that of silicon killed steels. At higher temperatures, rimmed steels lose creep strength more rapidly. Apparently the silicon and aluminum in deoxidized steels serve to immobilize the nitrogen. In rimmed steels, no "stabilizers" are present and nitrogen is less effective in reducing the strength.

The effect of nitrogen on the creep strength is related along parallel lines to the effect of this element on the strain aging tendencies at room and slightly elevated temperatures. However, both precipitation aging and strain aging phenomena were examined and neither of these mechanisms could be accepted without reservation. The results of these tests do indicate that the nitrogen is only effective in increasing the strength under conditions involving plastic deformation and that this change in strength is not accompanied by a change in hardness. A change in activation energy for creep corresponding to the change in dissolved nitrogen was noted, and the activation energy changed roughly by the same amount as the activation energy for the diffusion of nitrogen in iron. In light of a strain aging mechanism, this would indicate that the dislocations required more energy for the start of plastic flow. A maximum effect of active nitrogens was indicated at about 0.006 percent nitrogen and was roughly related to the number of dislocations in the steel. The true mechanism is apparently stress-controlled, and this stress is, in all probability, related to the increase in energy necessary to move the dislocations surrounded by nitrogen atmospheres. The energy for activation is probably the elastic strain energy corresponding to a "critical" stress. It is also probable that the nitrogen precipitated during test, as shown by Beeghly's method, is still in a form which interferes with the creep process since no change in creep rate was noted during the testing at 850° F. Considerably more research will be necessary before a clear-cut proposal of a mechanism is possible, and an approach to this study has been outlined. For the present, the mechanism involved is very closely allied to a strain aging mechanism, as outlined by Cottrell, but this mechanism cannot be fully accepted without reservation or further testing.

TABLES

TABLE I

CHEMICAL ANALYSES OF COMMERCIAL STEELS

Steel	C %	Mn %	P %	S %	Si %	Al %	Al_2O_3 %	Cr* %	Mo* %	Ni* %	Cu* %	N %
A	0.10	0.41	0.011	0.024	0.01	0.001	0.001	0.03	0.04	0.01	0.06	0.0040
B	0.15	0.43	0.016	0.031	0.18	0.024	0.004	0.05	0.01	0.03	0.08	0.0047
C	0.20	0.68	0.028	0.034	0.27	0.015	0.003	0.02	<0.05	0.02	0.10	0.0048
D	0.10	0.42	0.011	0.025	0.01	0.013	0.017	0.03	0.03	0.01	0.05	0.0038
E	0.10	0.43	0.010	0.025	0.01	0.047	0.019	0.03	0.03	0.01	0.06	0.0036
F	0.19	0.68	0.026	0.036	0.24	0.053	0.004	0.05	0.006	0.07	0.09	0.0046
H	0.15	0.50	0.011	0.035	0.01	<0.002	0.005	0.01	0.001	0.00	0.05	0.0125
J	0.19	0.82	0.010	0.019	0.16	0.029	0.013	0.03	0.003	0.00	0.05	0.0047

* Spectrographic Analysis

TABLE II

CHEMICAL ANALYSES OF VACUUM AND AIR MELTED STEELS

Steel	C %	Mn %	P %	S %	Si %	Al %	Al_2O_3 %	Cr* %	Mo* %	Ni* %	Cu* %	Zr %	N %
Air Melted													
1442	0.09	0.29	0.023	0.030	0.04	0.070	0.008	0.03	0.002	<0.01	0.09	.....	0.0098
1379	0.10	0.005	0.004	0.006	0.15	0.033	0.058	0.06	<0.05	0.00	0.00	.....	0.0089
Vacuum Melted													
1016	0.09	0.01	0.006	0.021	<0.06	0.01	.....	0.03	0.01	0.07	0.17	0.004	0.0014
1018	0.09	0.25	0.004	0.008	0.00	0.08	.....	0.03	0.005	0.03	0.00	0.002	0.0014
1019	0.09	0.05	0.004	0.012	0.44	0.06	.....	0.00	0.005	0.00	0.00	0.008	0.0017

* Spectrographic Analysis

TABLE III

AUSTENITIC GRAIN SIZE OF STEELS AT VARIOUS AUSTENITIZING TEMPERATURES*

Grain Size at	Steel										
	A	B	C	D	E	F	J	18	19	79	42
1650° F., 1 hr.	2-4	6-7	2-4	7-8	5-7	7-9	6-7(8)	5-7	1-3(5)	5-8(7)	6-8
1700° F., 10 hrs.	3-4(1)	7-8	1-2	3-4(6)	7-8	6-8	6-7	5-6(4)	1-2	6-8	6-8
1800° F., 1 hr.	......	...	...	......	......	......	......	4-5(7)	3-4	1-2(6)	7-8(9)
2000° F., 1 hr.	......	...	...	......	......	......	......	3-4	1-2(6)	3-5	3-5(6-7)
2150° F., 1 hr.	0-2	0-2	0-1	0-1	2-4(1)	1-2(4)	3-5	1-2(0)	1-2(0)	2-4(1)	2-4(6)

* Units: ASTM grain size determined for carburized specimens

TABLE IV

CREEP RATE AND DISSOLVED NITROGEN FOR DEOXIDIZED STEELS[a]

Steel Code	Austenitizing Temperature °F	Cooling Rate	Creep Rate %/hr.	Dissolved Nitrogen %
BFA	1650	A[b]	0.0026	0.0008
BFF	1650	F[c]	0.0057	0.0009
BCA	2150	A	0.000039	0.0032
BCF	2150	F	0.0040	0.0012
CFA	1650	A	0.000050	
			0.000029	0.0042
CFF	1650	F	0.000015	0.0042
CCA	2150	A	0.000025	0.0042
CCF	2150	F	0.000033	0.0042
			0.000025	0.0046
DFA	1650	A	0.000066	0.0029
DFF	1650	F	0.00275	0.0010
DCA	2150	A	0.000048	0.0035
DCF	2150	F	0.00021	0.0034
EFA	1650	A	0.0046	0.0001
EFF	1650	F	0.0039	0.0009
ECA	2150	A	0.000050	0.0031
ECF	2150	F	0.00295	0.0019
FFA	1650	A	0.00143	
			0.00080	0.0029
FFF	1650	F	0.00235	0.0008
FCA	2150	A	0.00005	0.0033
FCF	2150	F	0.00105	0.0025
JFA	1650	A	0.0035	0.0003
JFF	1650	F	0.00325	0.0002
JCA	2150	A	0.000069	0.0035
JCF	2150	F	0.00031	0.0018

[a] Creep tests conducted at 850° F. and 15,000 psi

[b] Air cooled

[c] Furnace cooled

TABLE V

ANALYSIS OF THE EFFECT OF HEAT-TREATMENT ON ALUMINUM AND ALUMINUM OXIDE IN ALUMINUM KILLED STEELS

Heat-Treatment	Steel					
	B		E		F	
	Al %	Al_2O_3 %	Al %	Al_2O_3 %	Al %	Al_2O_3 %
1650 A.C.	0.022	0.002	0.054	0.003	0.048	0.001
1650 F.C.	0.020	0.002	0.054	0.003	0.052	0.001
2150 A.C.	0.022	0.002	0.054	0.003	0.045	0.002
2150 F.C.	0.022	0.001	0.056	0.003	0.052	0.001

Analysis of Variance

Variable	Aluminum			Aluminum Oxide		
	F Ratio	Degrees Freedom	Significance	F Ratio	Degrees Freedom	Significance
Between Steels	1.91	3	<0.01	13.1	3	<0.01
Between Heat-Treatment	1.04	2	Not	2.12	2	Not
Residual	1.00	6	.....	1.00	6	.....

TABLE VI

CREEP RATES AND TOTAL NITROGEN FOR RIMMED STEELS[a]

Steel Code	Austenitizing Temperature °F	Cooling Rate	Creep Rate %/hr.	Total Nitrogen %
AFA	1650	A[b]	0.00021	0.0040
AFF	1650	F[c]	0.00036	0.0040
ACA	2150	A	0.00022	0.0040
ACF	2150	F	0.00046	0.0040
A Vacuum Annealed	2150	A	0.00236	0.00135
HFA	1650	A	0.000094	0.0125
HCA	2150	A	0.000031	0.0125
HCF	2150	F	0.000049	0.0125

[a] Creep tests conducted at 850° F. and 15,000 psi

[b] Air cooled

[c] Furnace cooled

TABLE VII

CREEP RATE AND DISSOLVED NITROGEN FOR STEELS IN THE AS-ROLLED CONDITION[a]

Steel	Rolling Conditions	Creep Rate %/hr.	Dissolved Nitrogen %
B[b]	Hot rolled from 2150° F.	0.00025	0.0047
B[b]	Hot rolled from 1750° F.	0.0050	0.0022
C	As Hot Rolled-Mill	0.000025	0.0046
F	As Hot Rolled-Mill	0.00011	0.0038
F	Hot Rolled-Mill and Stress Relieved 2 hrs. at 1150° F.	0.00085	0.0024

[a] Creep tests at 850° F. and 15,000 psi
[b] Retest after prior test at 10,000 psi and 850° F.

TABLE VIII

CREEP RATE AND DISSOLVED NITROGEN FOR SPHEROIDIZED AND UNSPHEROIDIZED CONDITIONS OF STEELS "C" AND "F"*

Sample Code	Spheroidization Treatment	Creep Rate %/hr.	Dissolved Nitrogen %
FFA	None	0.00143 0.00080	0.0029
FFAS	1250° F., 100 hrs.	0.00104	0.0012
FCA	None	0.000050	0.0033
FCAS	1250° F., 100 hrs.	0.00207	0.0010
CCA	None	0.000025	0.0042
CFAS	1250° F., 100 hrs.	0.00455	0.0006

*Creep tests were conducted at 850° F. and 15,000 psi

TABLE IX

CREEP RATE AND DISSOLVED NITROGEN FOR VACUUM MELTED AND VACUUM EXTRACTED STEELS[a]

Steel	Condition		Nitrogen %	Creep Rate %/hr.
	Austenitized °F	Cooled		
Vacuum Extracted				
C	1650	A[b]	0.0011	0.0060
C	2150	A	0.0016	0.00037
A	2150	A	0.00135	0.00236
Vacuum Melted				
1016	1650	A	0.00135	0.076
1018	1650	A	0.0014 0.0011	0.042
1018	2150	A	....	0.00632
1019	1650	A	0.0017 0.0017	0.400
1019	2150	A	....	0.210
Air Melted				
1379	1650	A	0.0012	0.222
1379	2150	A	0.0080	0.0004
1442	1650	A	0.0015 0.0048	0.0156
1442	2150	A	0.0036	0.00000756

[a] Creep tests were conducted at 850° F. and 15,000 psi

[b] Air cooled

TABLE X

HARDNESS OF DEOXIDIZED STEELS IN BASIC CORRELATION OF FIGURE 2

Steel and Heat-Treatment Code	Original Hardness Rockwell B	Hardness After Testing Rockwell B		Log Deviation From Correlation Curve x 10^3
		Reduced Section	Shoulder	
BFA	65.0	66	62	- 30
BFF	57.5	61	56	+271
BCA	63.5	. .	. .	-460
BCF	52.0	60	53	+395
CFA	75.0	72	70	+ 54
CFF	68.0	67	65	-252
CCA	75.5	73	75	- 21
CCF	69.0	73	70	+ 99
DFA	55.0	48	50	-760
DFF	41.5	48	39	+143
DCA	57.5	65	71	+ 6
DCF	38.0	40	37	+450
EFA	57.0	53	50	-167
EFF	53.0	53	52	- 24
ECA	58.0	50	46	-352
ECF	40.0	69	45	+559
FFA	75.5	74	74	+734
FFF	74.0	70	70	- 74
FCA	74.5	72	71	-233
FCF	68.0	70	69	+586
JFA	75.0	66	67	-281
JFF	71.0	63	66	-289
JCA	77.5	45	43	- 4
JCF	72.0	57	60	-330

TABLE XI

HARDNESS OF RIMMED AND OTHER STEELS TESTED

Steel and Heat-Treatment Code	Original Hardness Rockwell B		Hardness After Test	
			Reduced Section	Shoulder
	Rim	Core		
AFA	52	65	61	58
AFF	38	48	43	51'
ACA	51	64	. .	. .
ACF	38	50	. .	. .
A, Extracted	53		. .	. .
HFA	65		66	66
HCA	64		63	63
HCF	. .		56	54
C, As-Rolled	. .		72	73
CFA, Extracted	70		. .	. .
CCA, Extracted	73		. .	. .
F, As-Rolled	72		. .	. .
F, Stress Relieved	69		. .	. .
FFA, Spheroidized	. .		67	64
FCA, Spheroidized	69		62	63
CFA, Spheroidized	60		67	63
1016 FA	49		58	39
1018 CA	53		58	51
1018 FA	58		61	48
1019 CA	60		67	54
1019 FA	64		70	59
1379 CA	54		53	45
1379 FA	52		57	46
1442 CA	59		. .	. .
1442 FA	62		. .	. .

TABLE XII

MEASUREMENT OF ALUMINUM NITRIDE BEFORE AND AFTER TESTING AT 850° F. FOR TIMES UP TO 1660 HOURS

Steel and Time of Test	Percent Nitrogen as Aluminum Nitride		
	As Heat-Treated	After Test at Times 850° F.	Change in AlN, %
F Stress Relieved, 763 hrs.	0.0022	0.0031	+0.0009
F As-Rolled, 1661 hrs.	0.0008	0.0022	+0.0014
FCA, 1292 hrs.	0.0013	0.0028	+0.0015
BCA, 1240 hrs.	0.0016	0.0023	+0.0007
FFA, 858 hrs.	0.0019	0.0032	+0.0013
AFA, 710 hrs.	......	0.0004	....
DFA, 688 hrs.	0.0009	0.0014	+0.0005
ECA, 600 hrs.	0.0007	none detected	....

TABLE XIII

SUMMARY OF ACTIVATION ENERGIES FOR CREEP TESTS ON PLAIN CARBON STEEL

Temp. °F	ΔH Act. Cal/Mole	Type Steel	Method	Significance
850	13,900	Rimmed Steels	Dorn: (40) T Const. Intercept to Max. N_2	Represents ΔH Difference Due to Nitrogen
850	16,500	All Deoxidized Commercial Steels	Dorn: T Const. Intercept to Max. N_2	Represents ΔH Difference Due to Nitrogen
850	21,000	Steel 1379	Dorn: T Const. Intercept to Max. N_2	Represents ΔH Difference Due to Nitrogen
800 - 900	112,000	High Nitrogen Steels	Dorn: T Variable, % N Constant	Activation Energy Iron + Nitrogen
800 - 900	82,000	Low Nitrogen Steels	Dorn: T Variable, % N Constant	Activation Energy Iron
1000-1400	90,000	0.15% C (40)	Dorn: T Variable, (Rupture)	Activation Energy Iron
900 -1200	137,500	(High Nitrogen)(7) Coarse Grained	Dorn: T Variable	Activation Energy Iron + Nitrogen

FIGURES

DEOXIDIZED STEELS:
0.004-0.005 % NITROGEN

NOMINAL SILICON CONTENT	ALUMINUM ADDED		
	0 AL	1#AL T.	2#AL T.
0 Si	SEE RIMMED STEELS:	STEEL D 0.013 AL 0.01 Si	STEEL E 0.047 AL 0.01 Si
0.25 Si	STEEL C 0.015 AL 0.27 Si	STEEL J 0.029 AL 0.16 Si	STEEL F 0.053 AL 0.24 Si
		STEEL B 0.024 AL 0.18 Si	

RIMMED STEELS:

STEEL	% NITROGEN
A 0.001 AL 0.01 Si	0.004
H 0.001 AL 0.01 Si	0.0125
A VAC ANN	0.0014

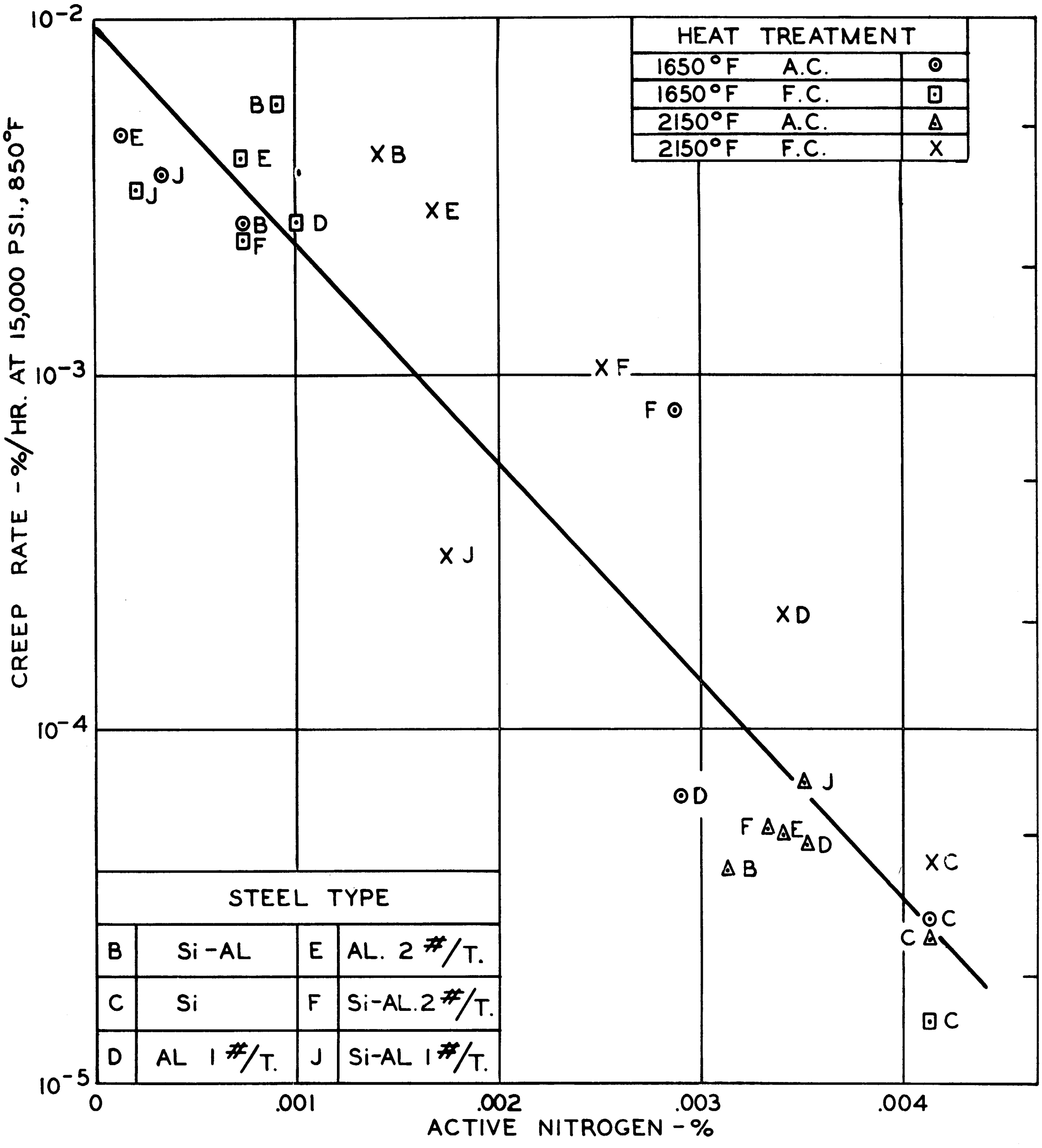
HEAT TREATMENT DESIGN AND CODE:

COOLING RATE	AUSTENITIZING TEMPERATURE	
	1650°F 1 HR.	2150°F 1 HR.
AIR COOL	*——— FA	*——— CA
FURNACE COOL	*——— FF	*——— CF

* STEEL DESIGNATION

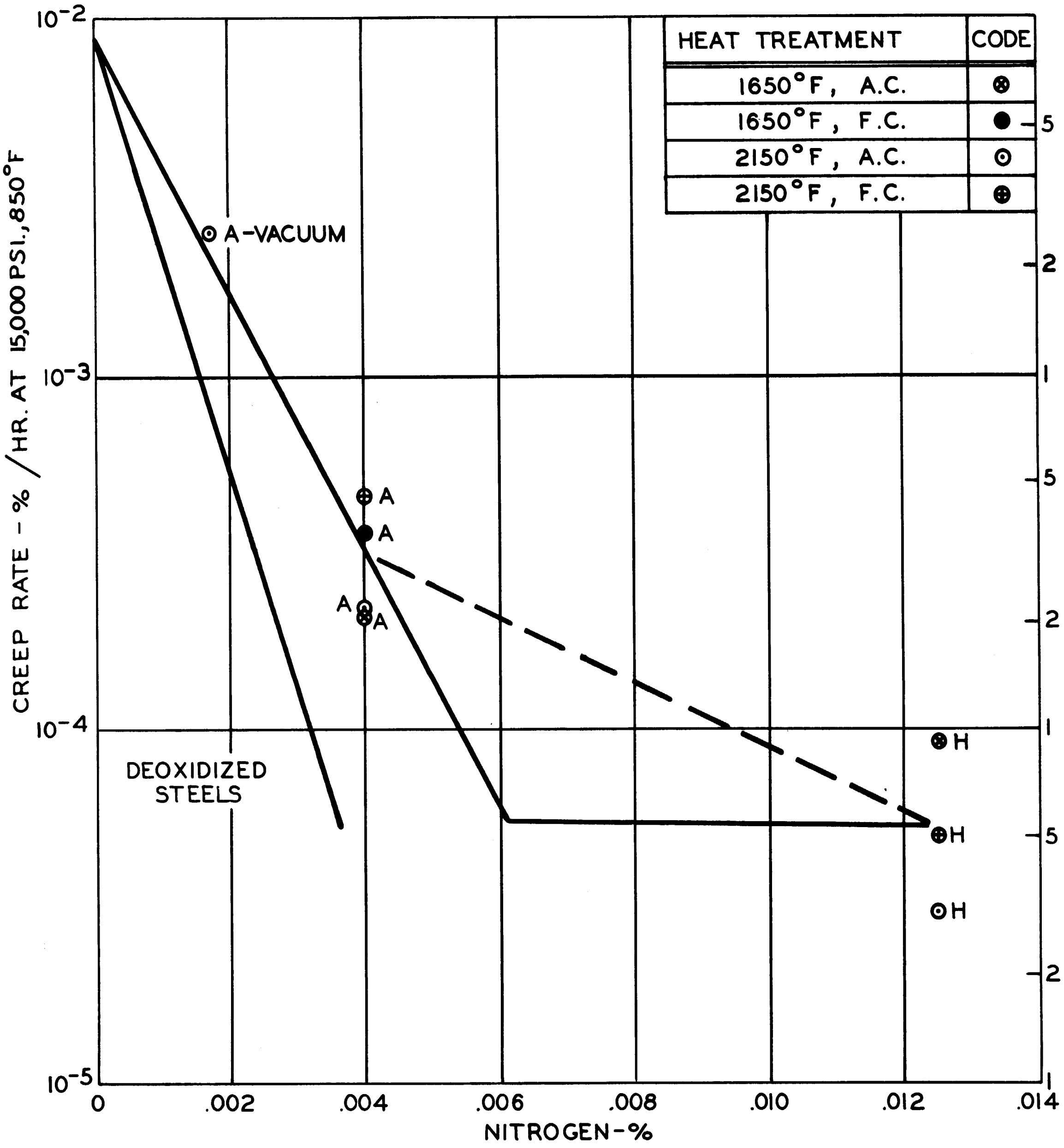
DESIGN OF BASIC EXPERIMENT FOR COMMERCIAL MATERIALS SHOWING NOMINAL AND ACTUAL ALUMINUM AND SILICON CONTENTS

FIGURE 1



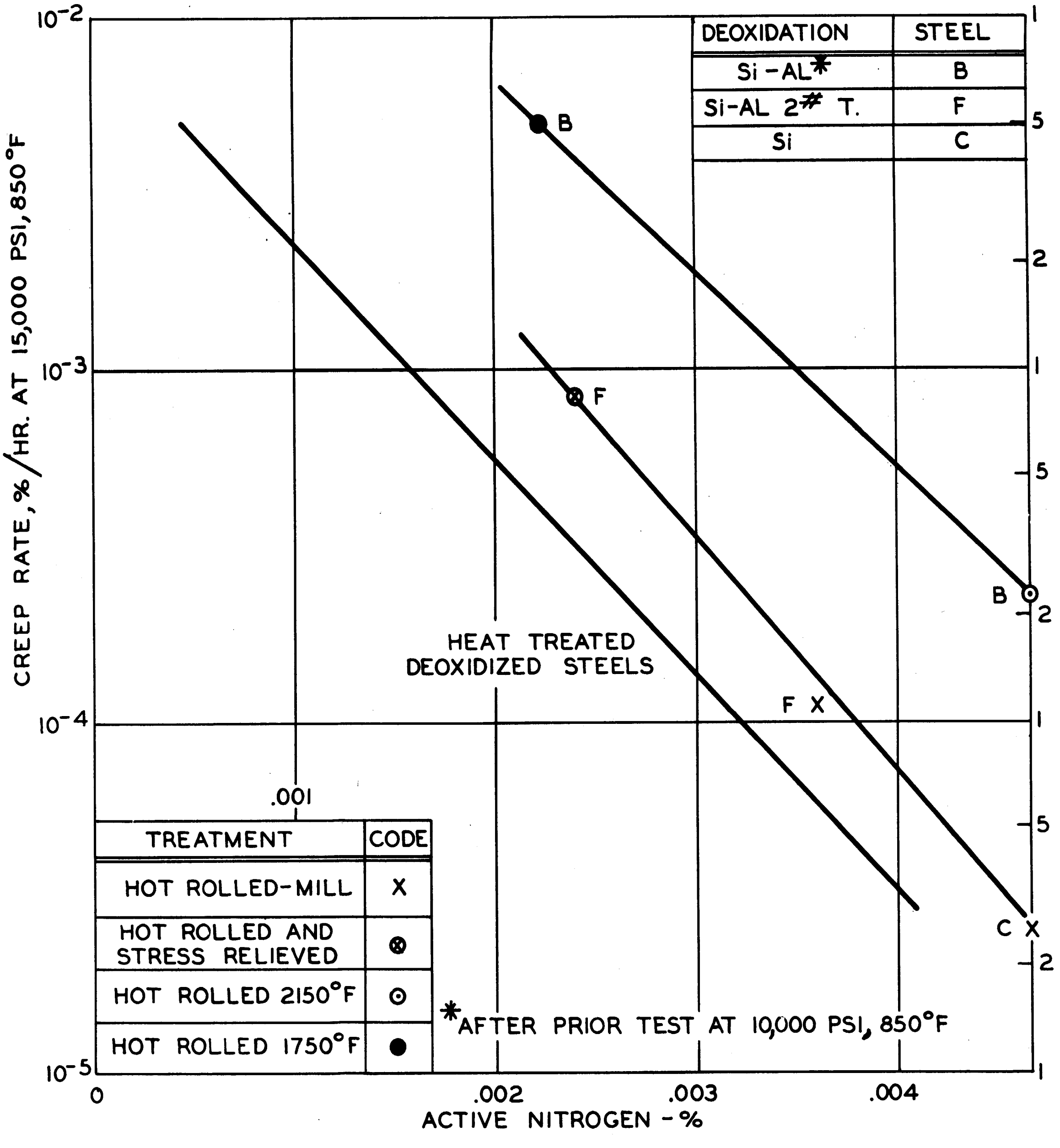
CORRELATION OF CREEP RATE WITH ACTIVE NITROGEN FOR DEOXIDIZED STEELS.

FIGURE 2



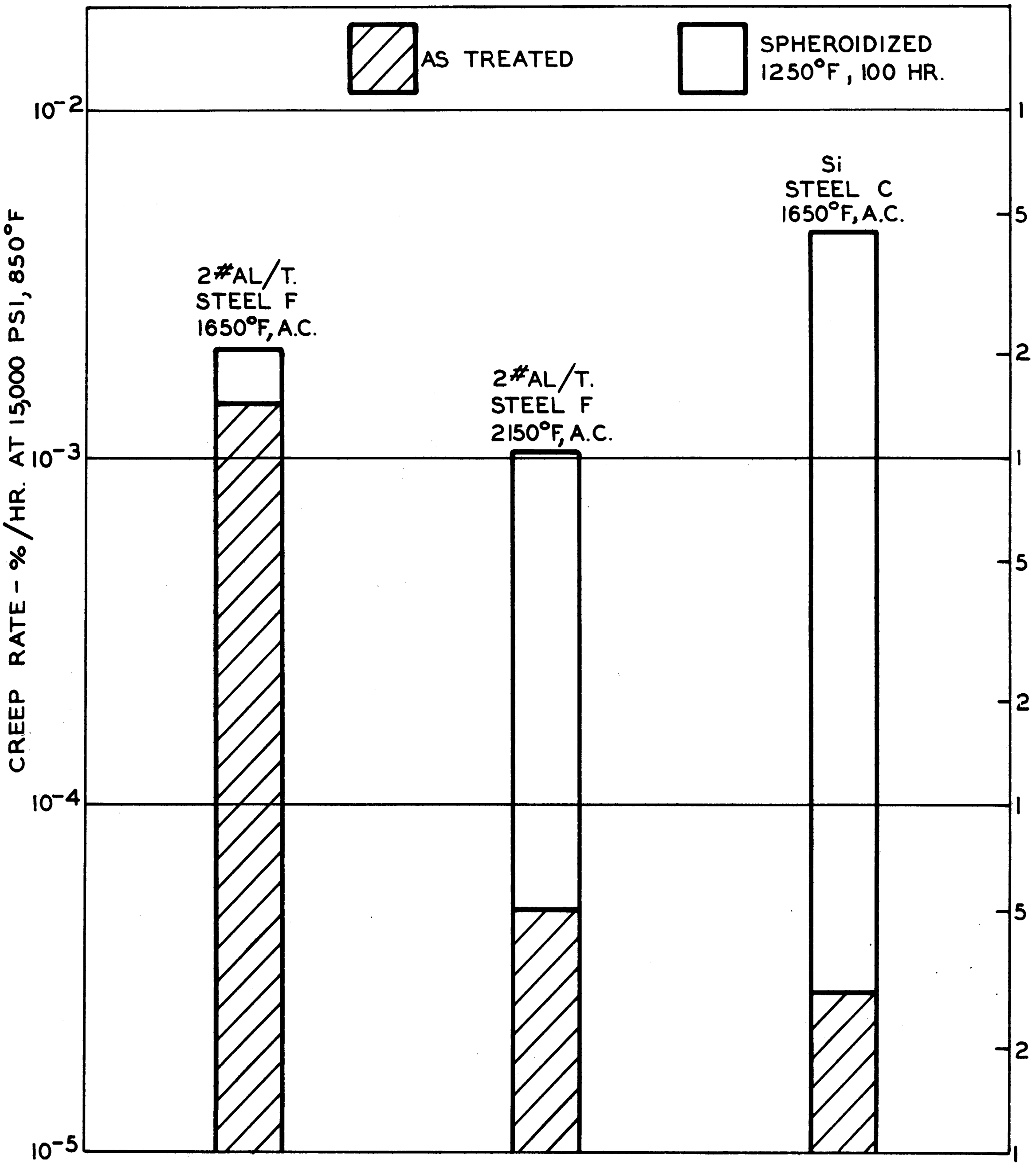
EFFECT OF NITROGEN ON THE CREEP STRENGTH OF RIMMED STEELS

FIGURE 3



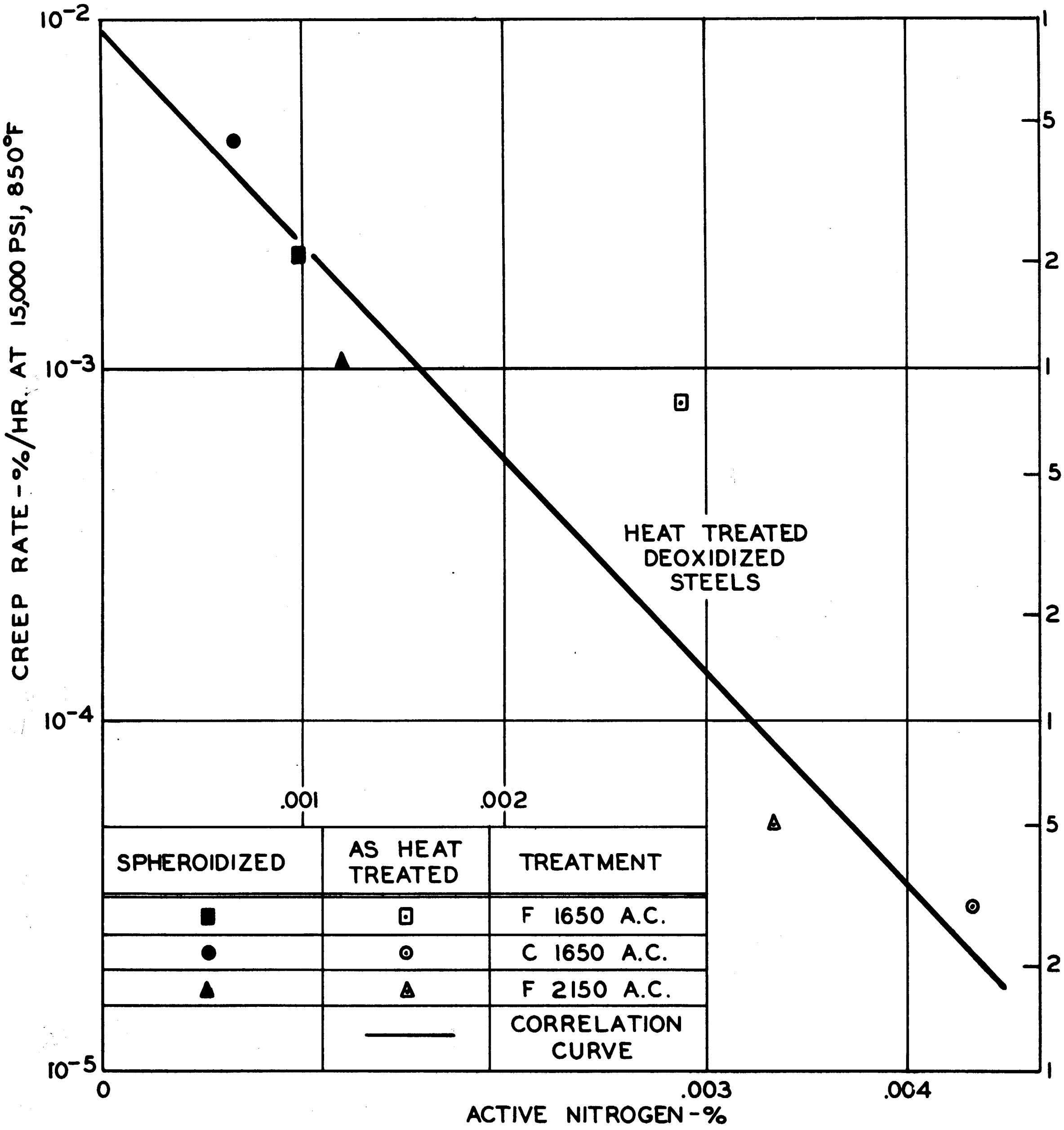
EFFECT OF ACTIVE NITROGEN ON THE CREEP STRENTH OF AS ROLLED OR STRESS RELIEVED PLAIN CARBON STEEL

FIGURE 4



EFFECT OF SPHEROIDIZATION ON CREEP STRENGTH OF FINE AND COARSE GRAINED STEELS

FIGURE 5

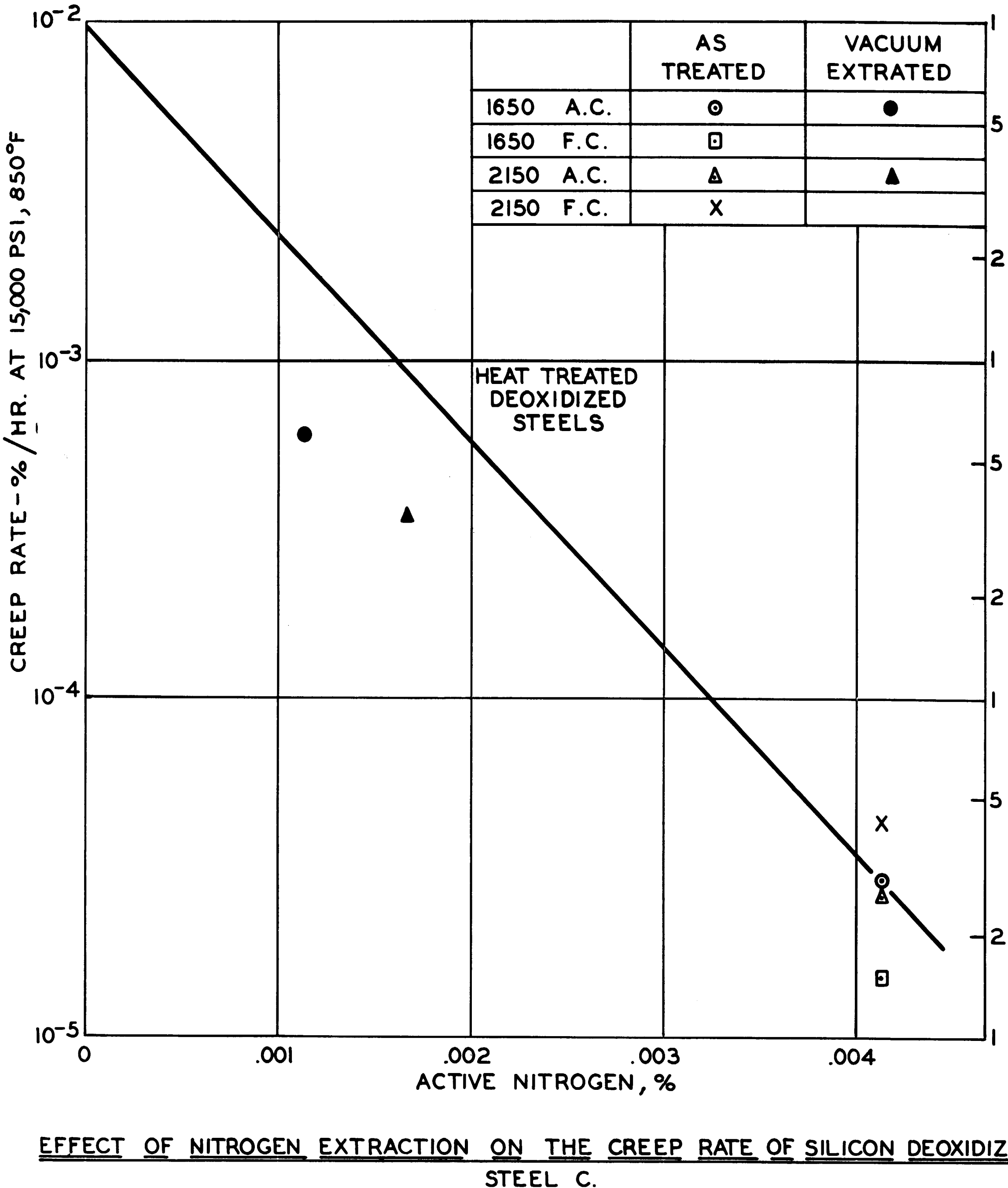


RELATION BETWEEN DISSOLVED NITROGEN AND CREEP RATE BEFORE AND AFTER SPHEROIDIZATION.

FIGURE 6

FIGURE 7: MICROSTRUCTURE OF VACUUM EXTRACTED SAMPLE OF SILICON-KILLED STEEL C

VACUUM EXTRACTION	100 HR. AT 2000°F.
HEAT TREATMENT	1650°F AIR COOL, THEN, 2150°F AIR COOL.
MAGNIFICATION	100 X
ETCHANT	NITAL
CREEP RATE	0.00037 %/HR.



EFFECT OF NITROGEN EXTRACTION ON THE CREEP RATE OF SILICON DEOXIDIZED STEEL C.

FIGURE 8

EFFECT OF NITROGEN ON THE DEOXIDATION-HEAT TREATMENT RELATION FOR STEELS WITH LOW AND HIGH NITROGEN

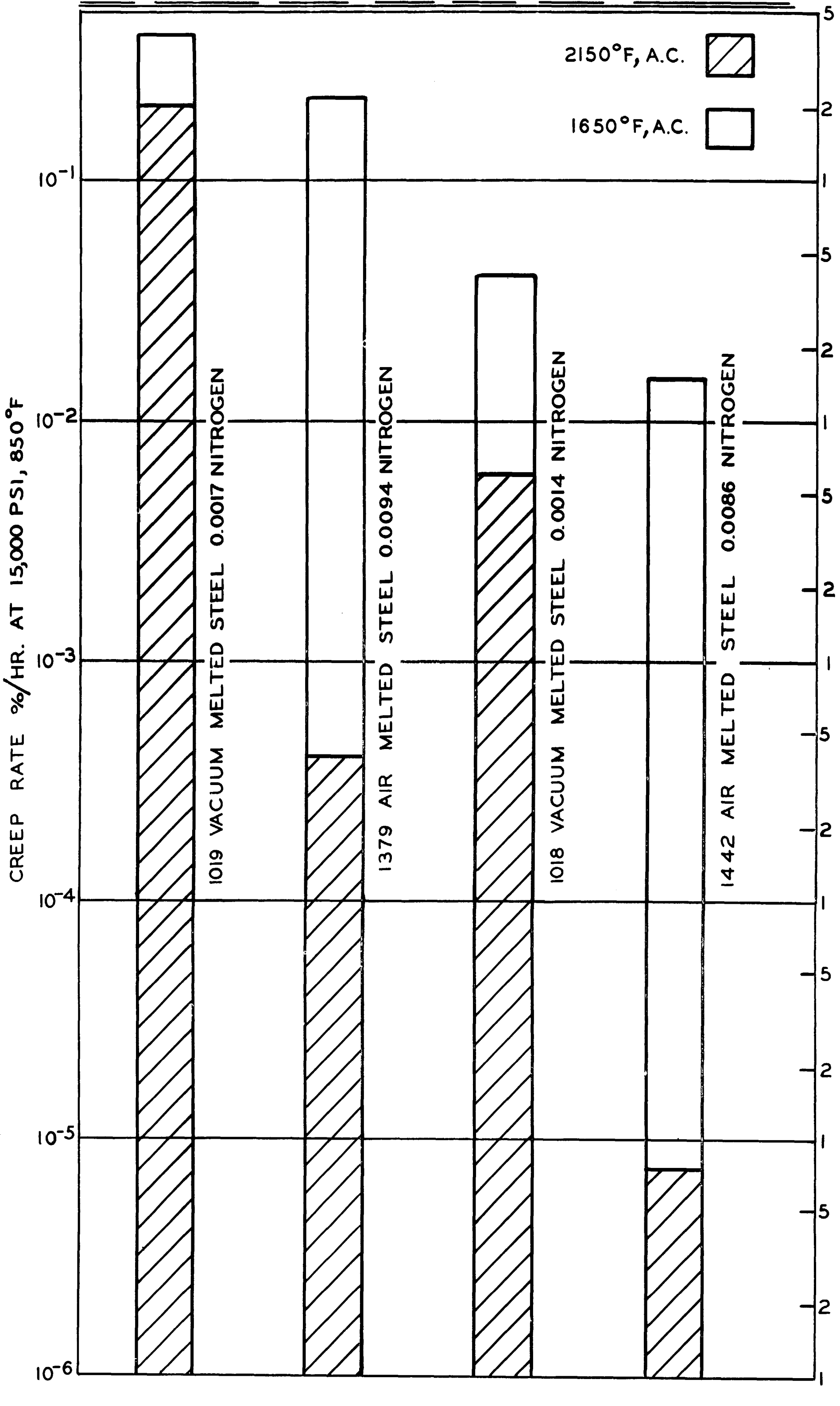
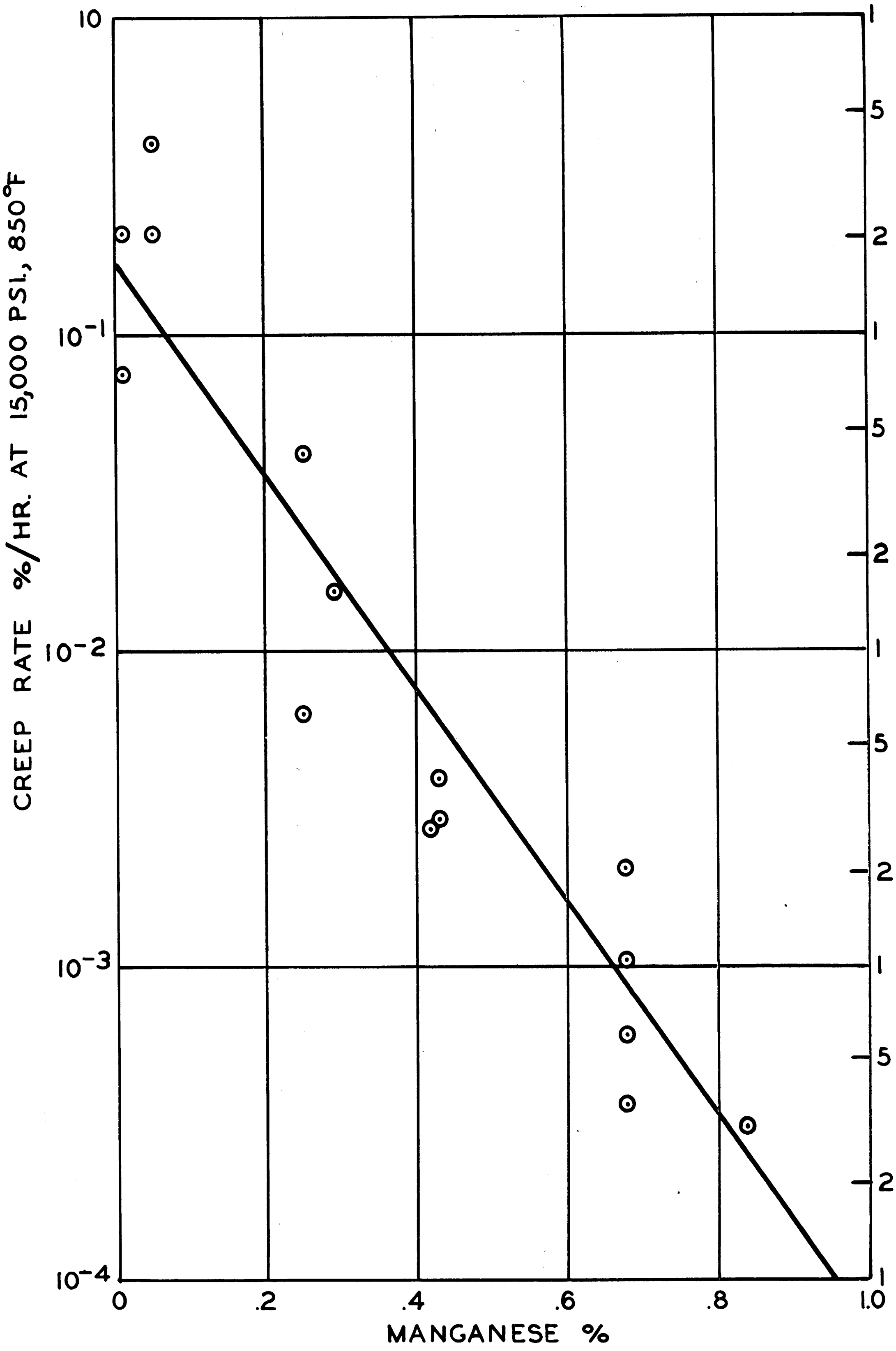
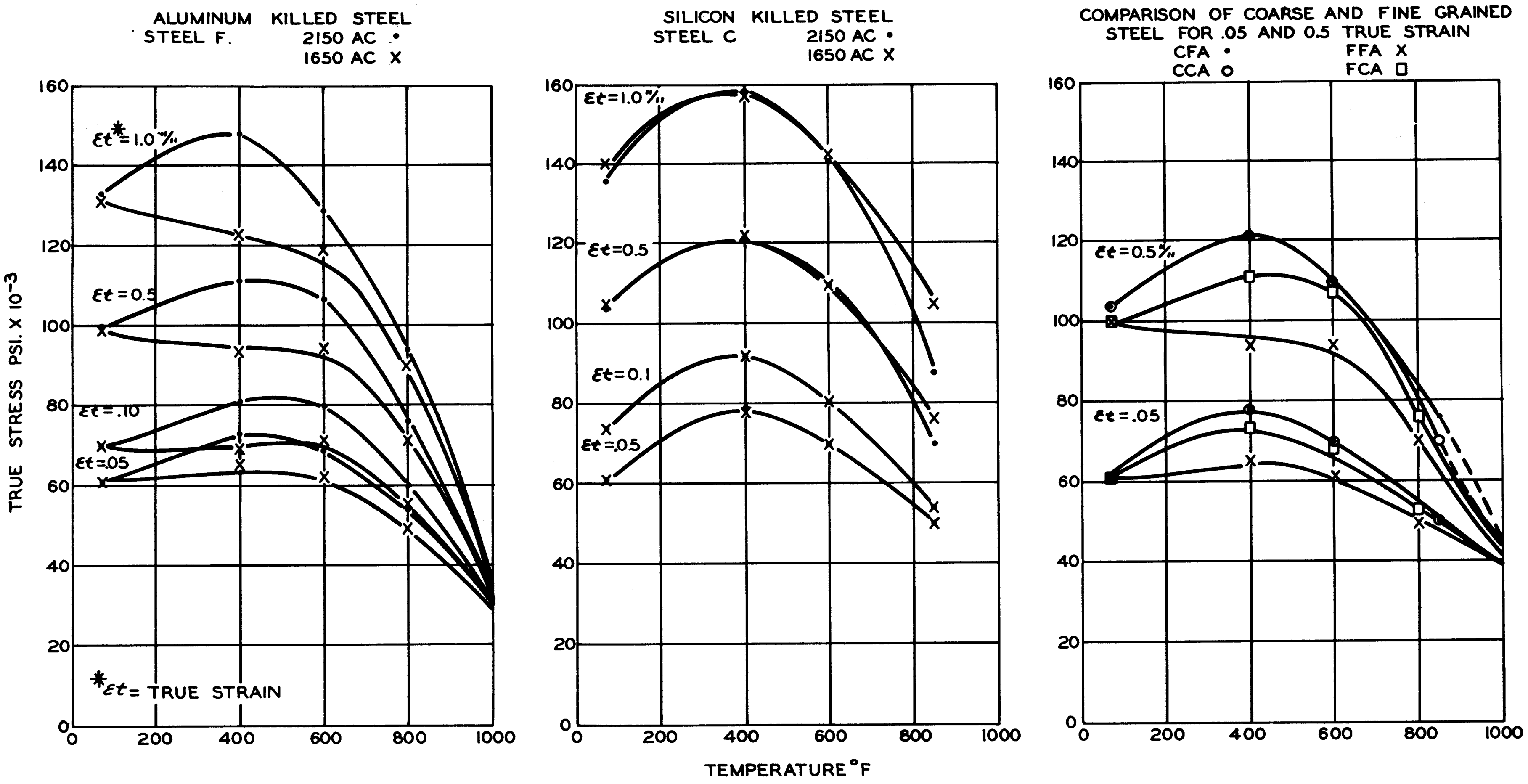


FIGURE 9



MANGANESE EFFECT FOR STEELS WITH 0.001 TO 0.002 % NITROGEN.

FIGURE 10



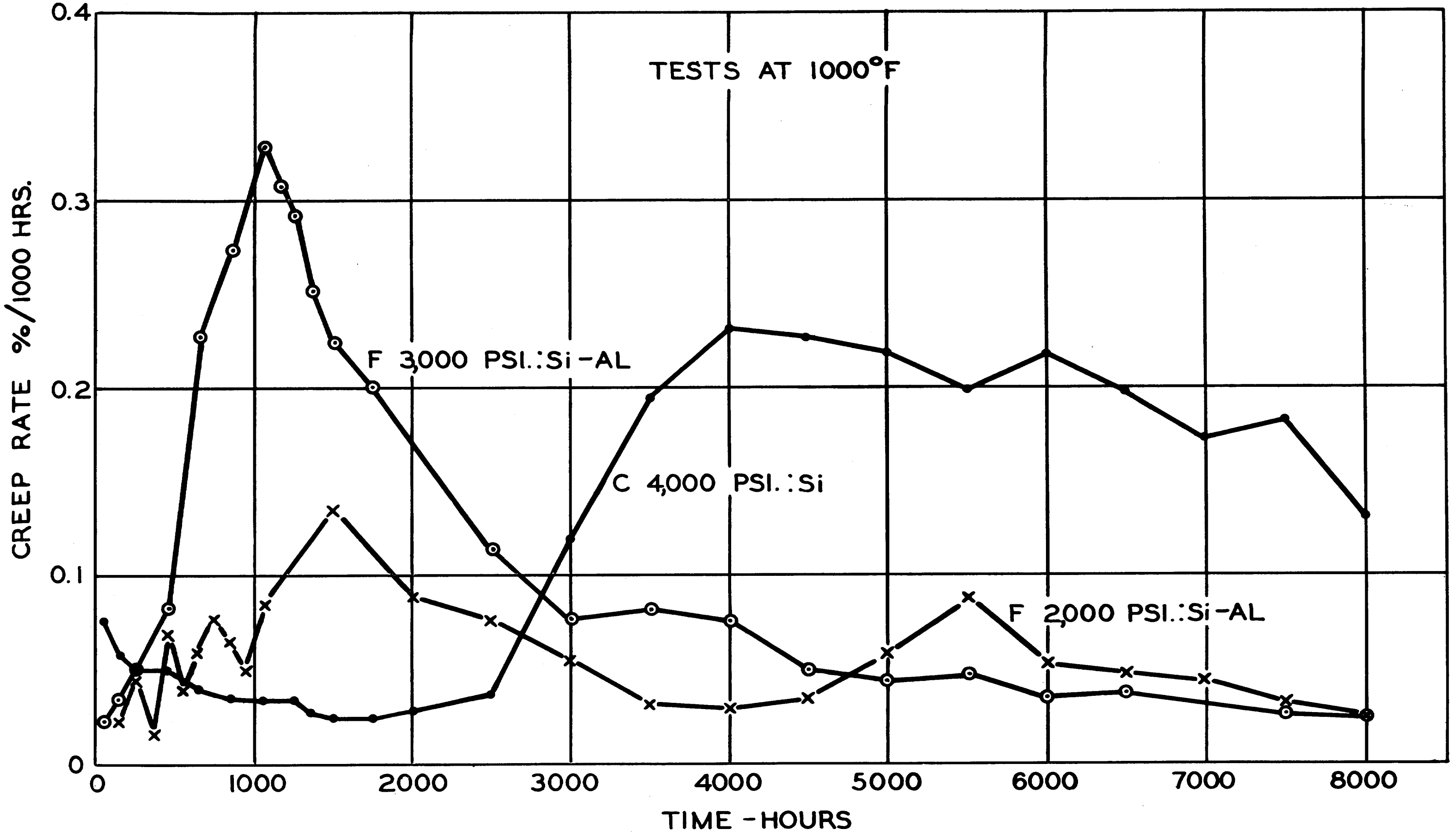
ALUMINUM KILLED STEEL
STEEL F. 2150 AC •
1650 AC X

SILICON KILLED STEEL
STEEL C 2150 AC •
1650 AC X

COMPARISON OF COARSE AND FINE GRAINED STEEL FOR .05 AND 0.5 TRUE STRAIN
CFA • FFA X
CCA o FCA □

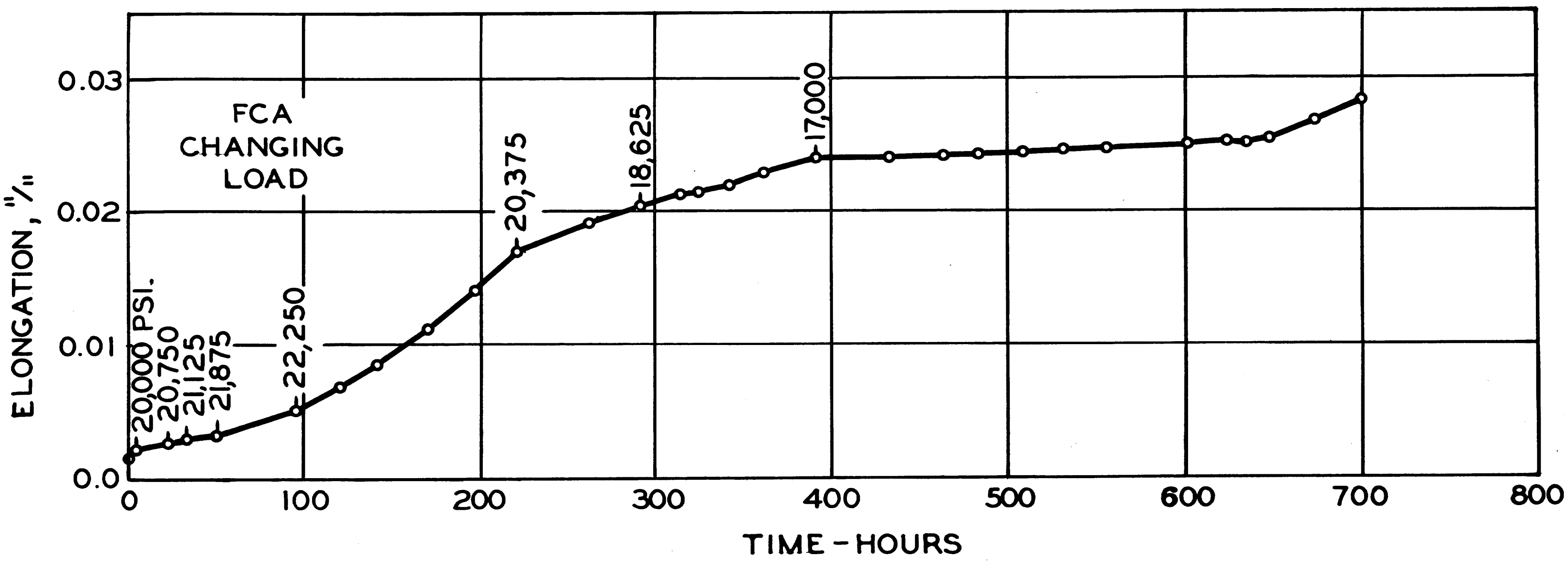
ISOSTRAIN CURVES FOR STEELS C AND F IN FINE AND COARSENED CONDITIONS.

FIGURE 11



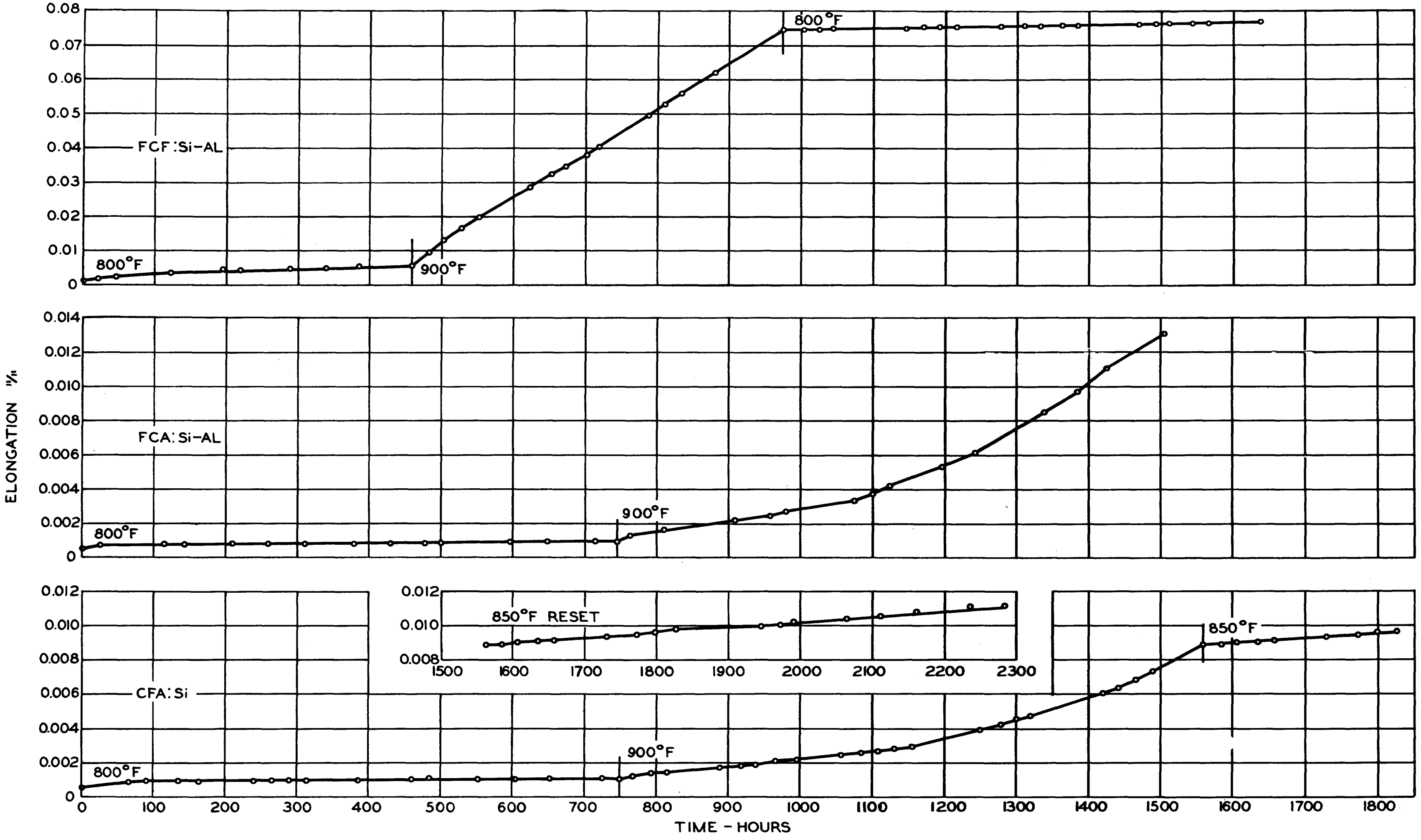
CREEP RATE-TIME PLOT FOR STEEL "C" AND "F" IN THE STRESS RELIEVED CONDITION AT 1000°F

FIGURE 12



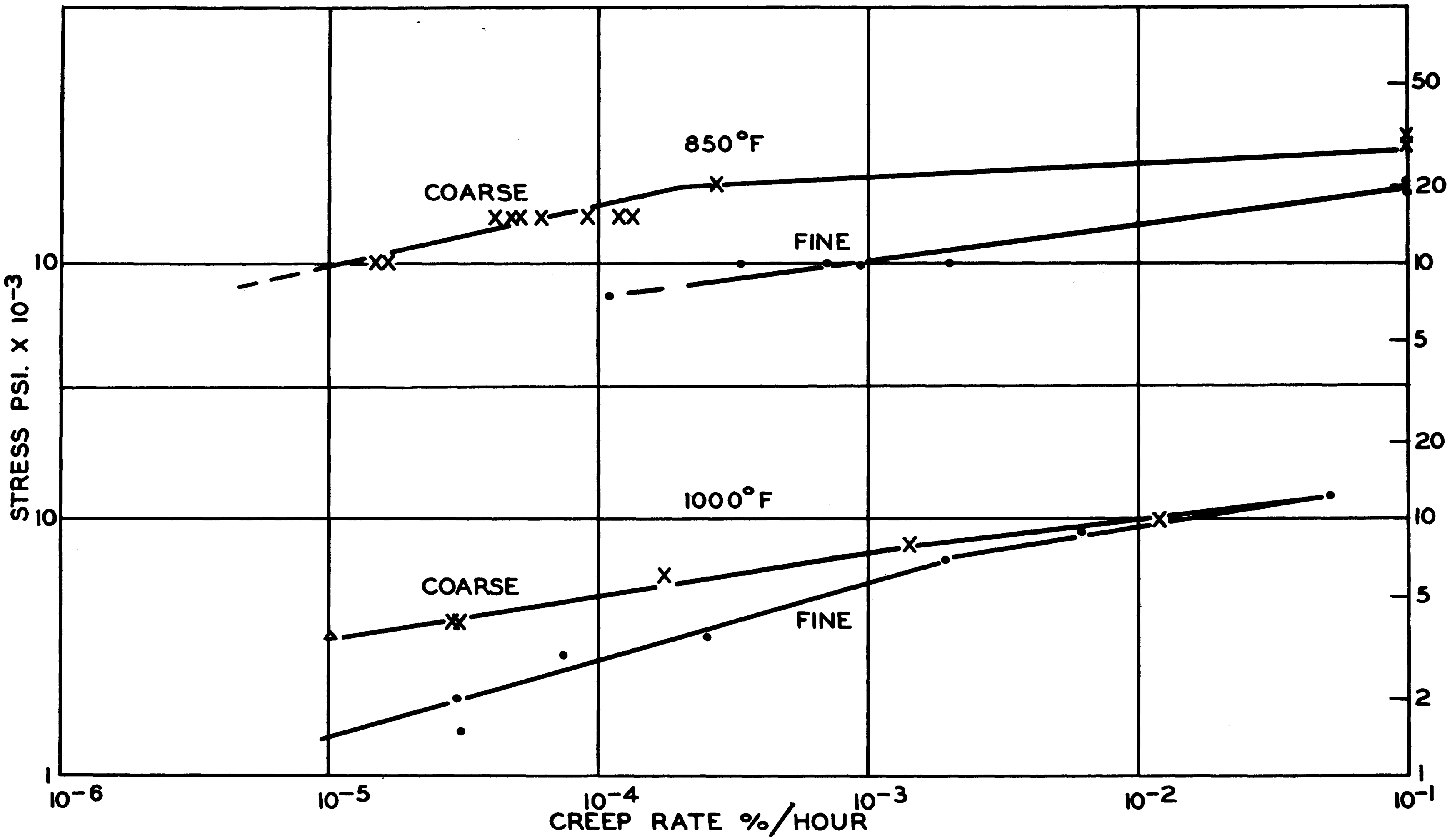
CREEP TEST WITH VARIABLE STRESS AT 850° F

FIGURE 13



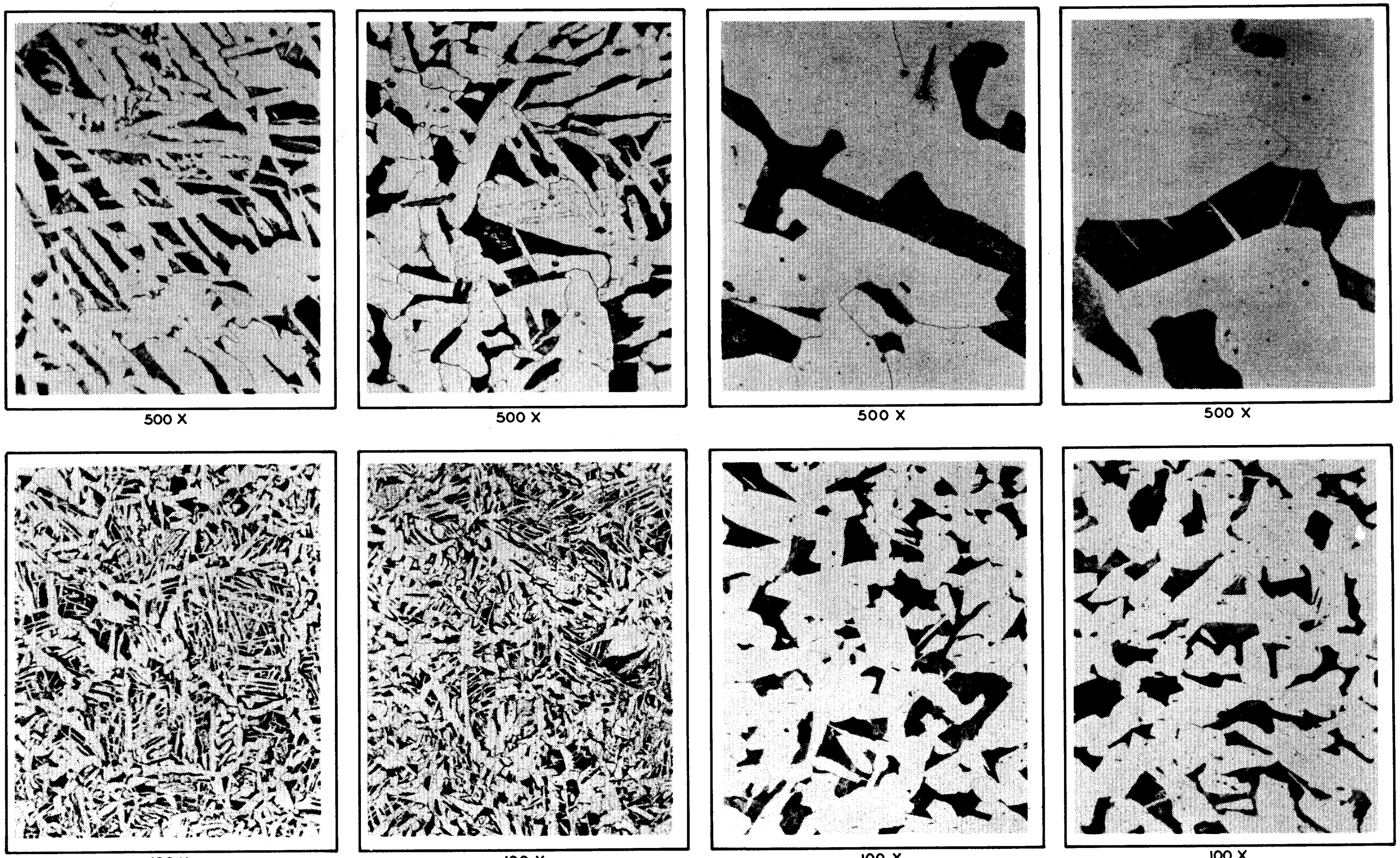
CREEP TESTS AT CONSTANT STRESS, VARIABLE TEMPERATURE

FIGURE 14



STRESS-CREEP RATE CURVES AT 850°F AND 1000°F FOR COARSE GRAINED (HIGH NITROGEN) AND FINE GRAINED (LOW NITROGEN) STEELS (3,8,9,10,13,14)

FIGURE 15



CCA: SILICON - KILLED STEEL: CREEP RATE 0.000025 %/HR.

FCA: SILICON-ALUMINUM KILLED STEEL, 2#/T: CREEP RATE 0.00005 %/HR.

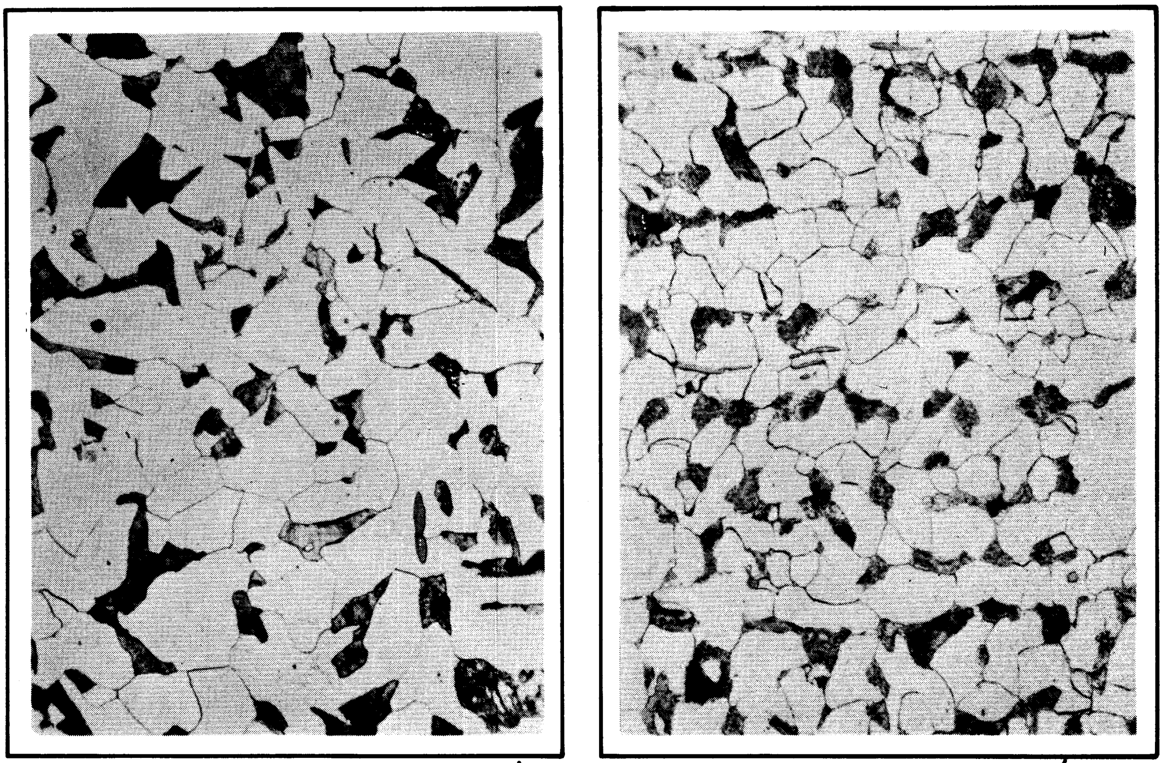
CCF: SILICON - KILLED STEEL CREEP RATE 0.000033 %/HR.

FCF: SILICON-ALUMINUM KILLED STEEL, 2#/T: CREEP RATE 0.00105 %/ HR.

FIGURE 16 ; MICROSTRUCTURES OF SILICON KILLED STEEL "C" AND SILICON ALUMINUM KILLED STEEL "F", AIR AND FURNACE COOLED FROM 2150°F, NITAL ETCH.

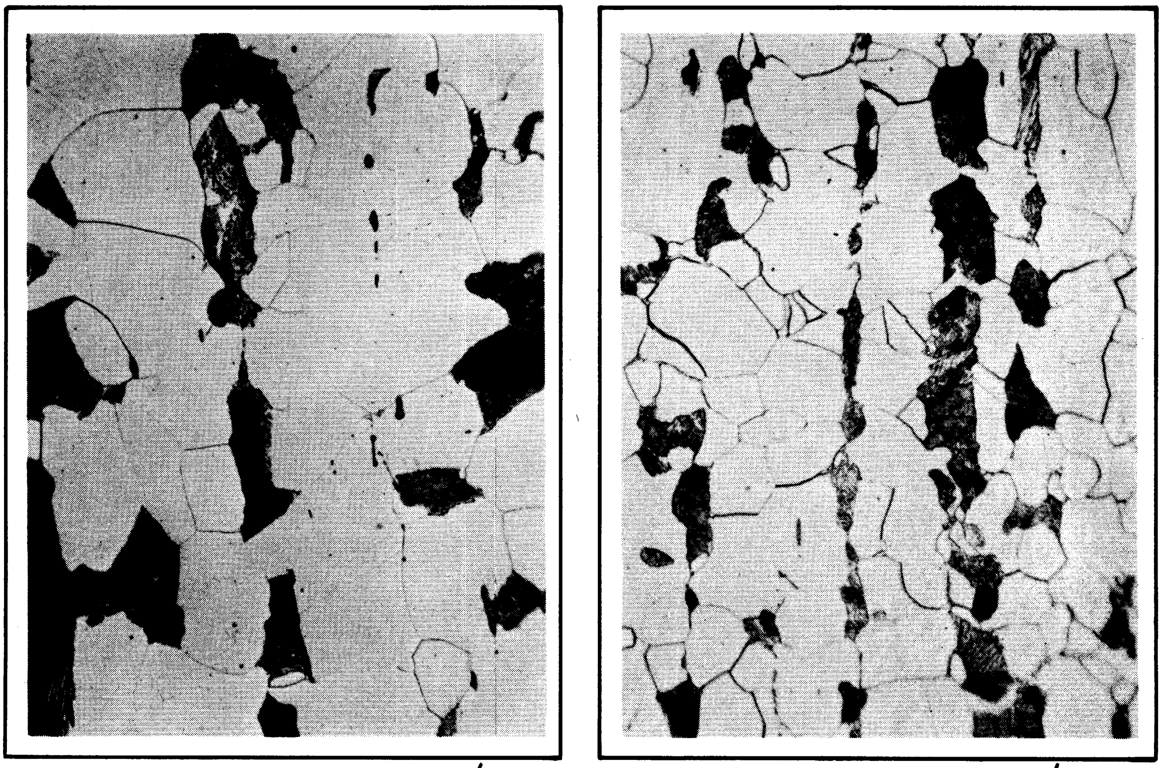
STEEL C: Si

STEEL F: Si -Al



CFA: CREEP RATE 0.000029 %/HR.

FFA: CREEP RATE 0.00080 %/HR.



CFF: CREEP RATE 0.000015 %/HR.

FFF: CREEP RATE 0.00235 %/HR.

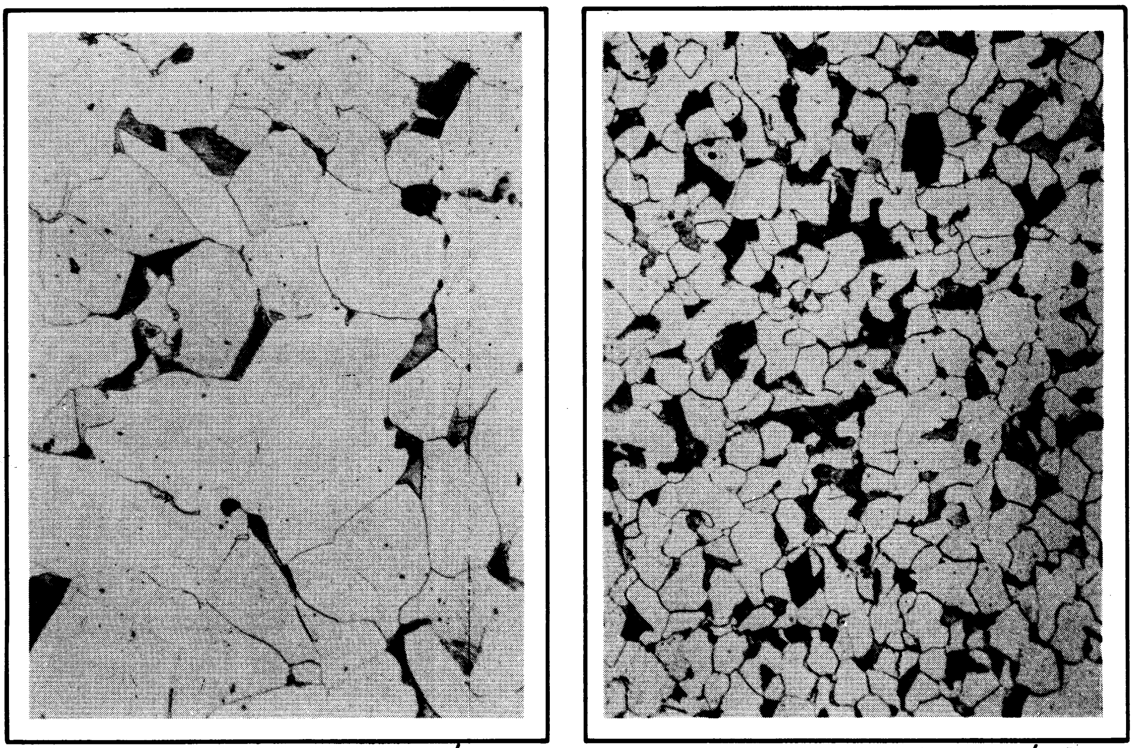
FIGURE 17: STEELS "C" AND "F" AFTER AIR AND FURNACE COOLING FROM 1650°F, NITAL ETCH, MAGNIFICATION 500 X.

STEEL D
0.10 % CARBON
AL 1#/T

STEEL J
0.19% CARBON
Si-AL 1#/T

DCA: CREEP RATE 0.000048 %/HR.

JCF: CREEP RATE 0.00031 %/HR.



DFA: CREEP RATE 0.00066 %/HR.

JFA: CREEP RATE 0.0035 %/HR.

FIGURE 18: TYPICAL MICROSTRUCTURES OF HIGH AND LOW RANGE OF CARBON CONTENT, NITAL ETCH, MAGNIFICATION 500 X

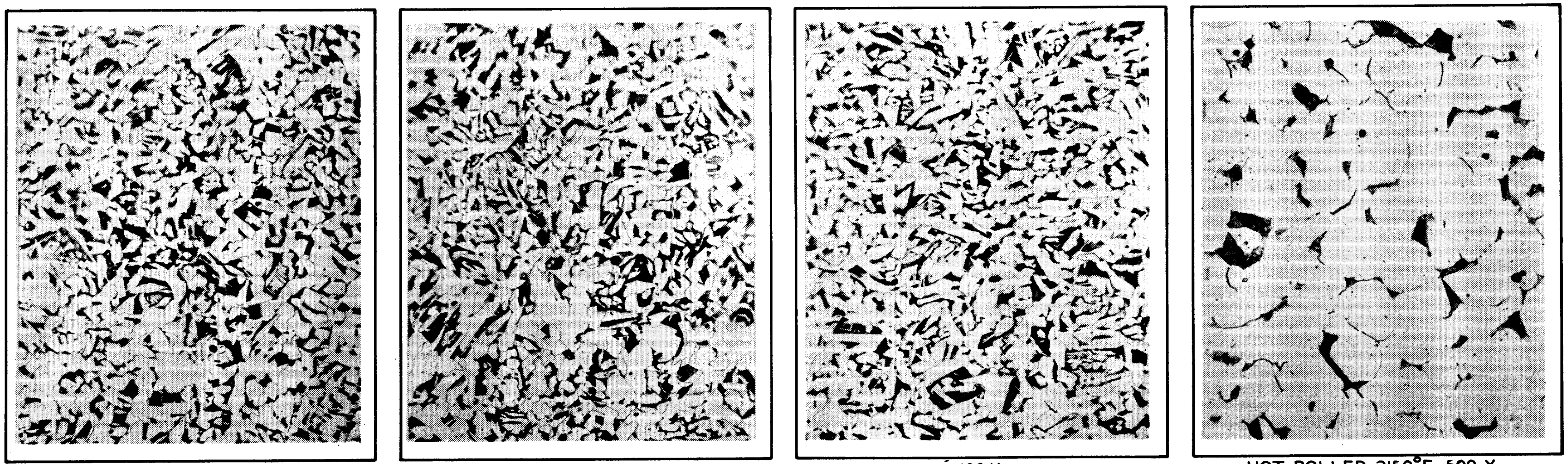
STEEL F-Si-AL | STEEL F-Si-AL | STEEL C-Si | STEEL B-Si-AL

500 X

500 X

500 X

HOT ROLLED 1750°F, 500 X
CREEP RATE 0.0050 %/HR.



100 X
AS ROLLED-MILL, STRESS RELIEVED
1150°F 2 HR, CREEP RATE 0.00085 %/HR.

100 X
AS ROLLED-MILL
CREEP RATE 0.00011 %/HR.

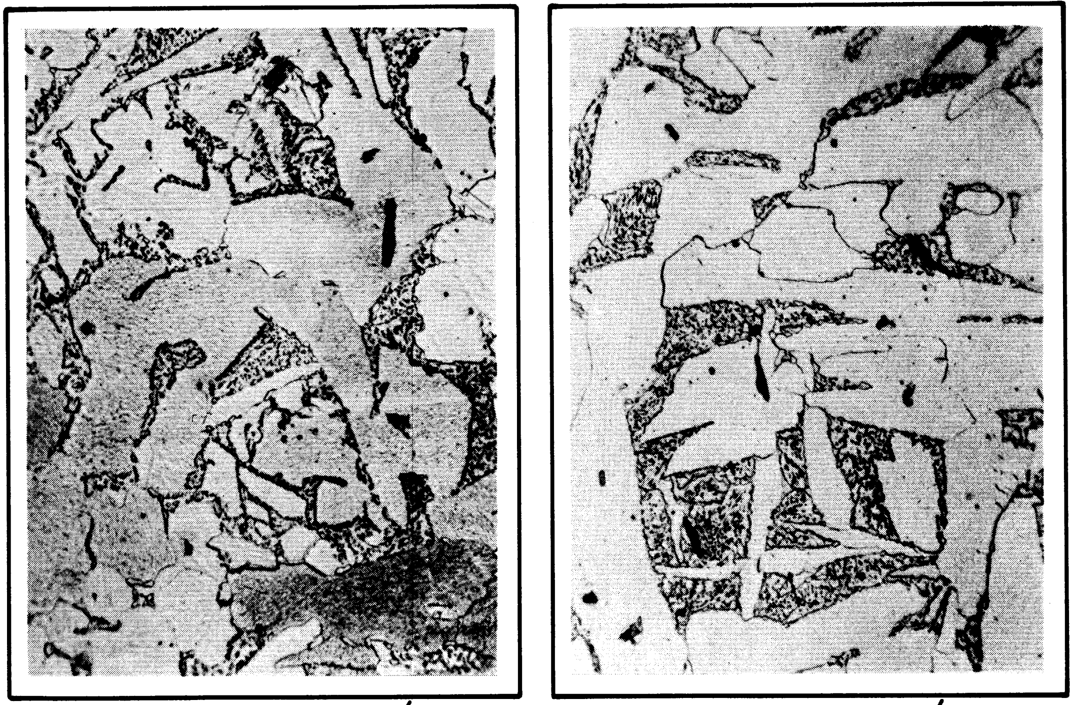
100 X
AS ROLLED-MILL
CREEP RATE 0.000025 %/HR.

HOT ROLLED 2150°F, 500 X
CREEP RATE 0.00025 %/HR.

FIGURE 19: MICROSTRUCTURES OF MATERIALS TESTED IN AS ROLLED CONDITION, NITAL ETCH.

STEEL C: Si 2150°F, A.C.
THEN 1250°F, 100 HRS.

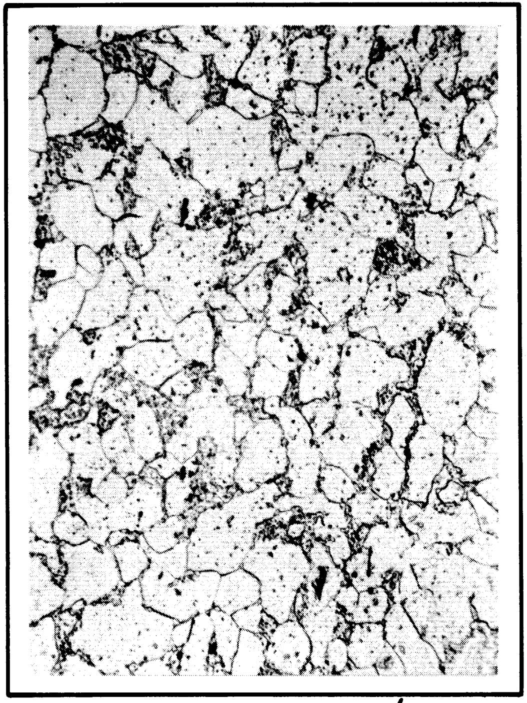
STEEL F: Si-AL, 2150°F, A.C.
THEN 1250°F, 100 HRS.



CREEP RATE 0.0045 %/HR.

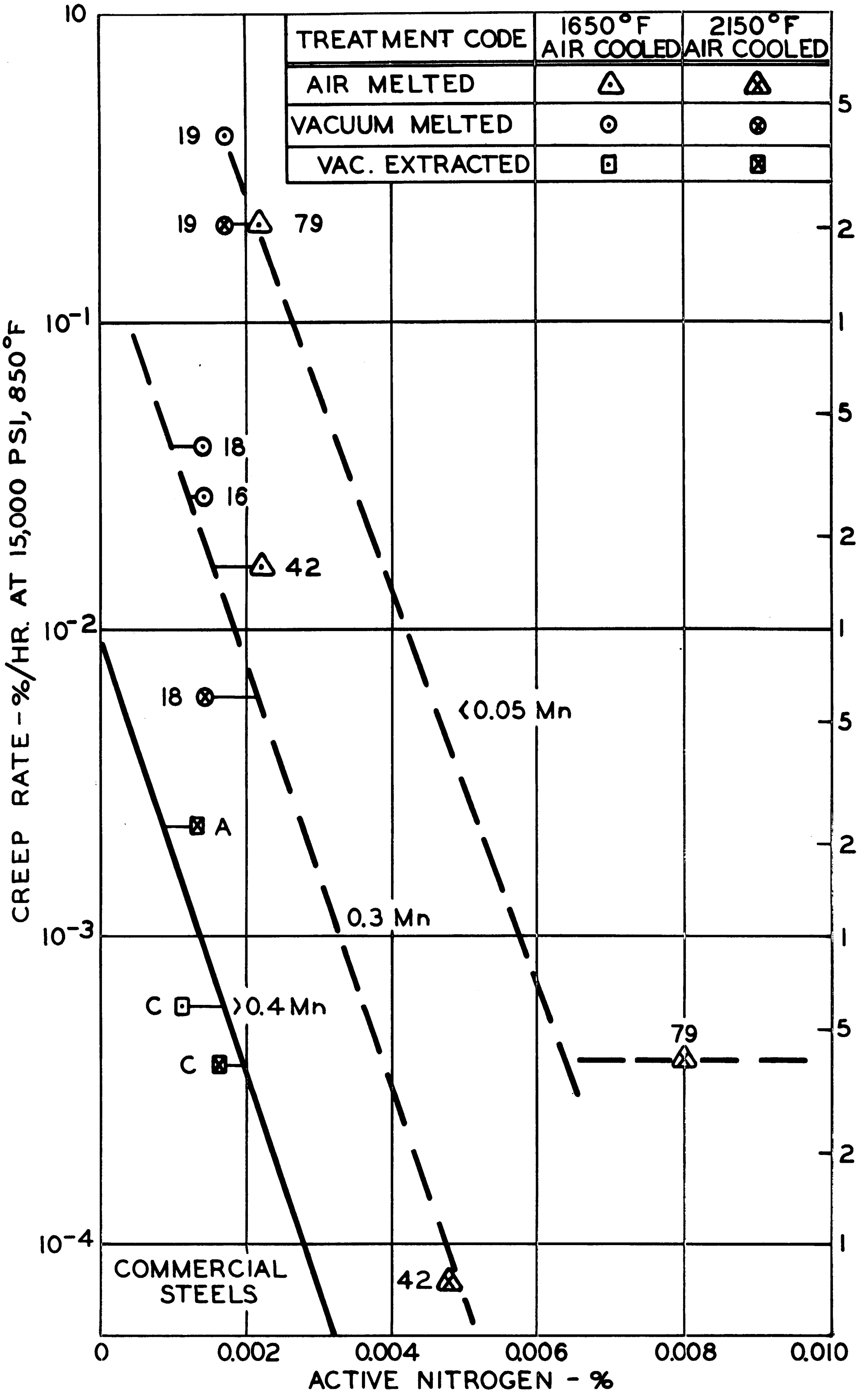
CREEP RATE 0.0010 %/HR.

STEEL F: Si-AL, 1650°F, A.C.
THEN 1250°F, 100 HRS.



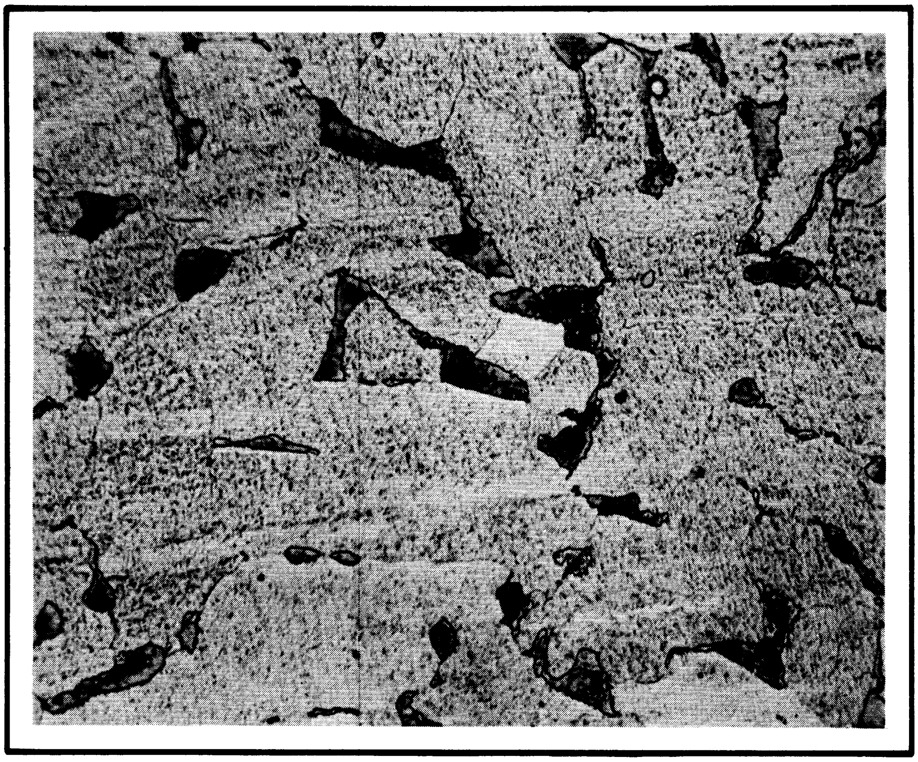
CREEP RATE 0.0021 %/HR.

FIGURE 20: MICROSTRUCTURES OF STEELS "C" AND "F" IN SPHEROIDIZED CONDITION, NITAL ETCH, MAGNIFICATION 500 X.

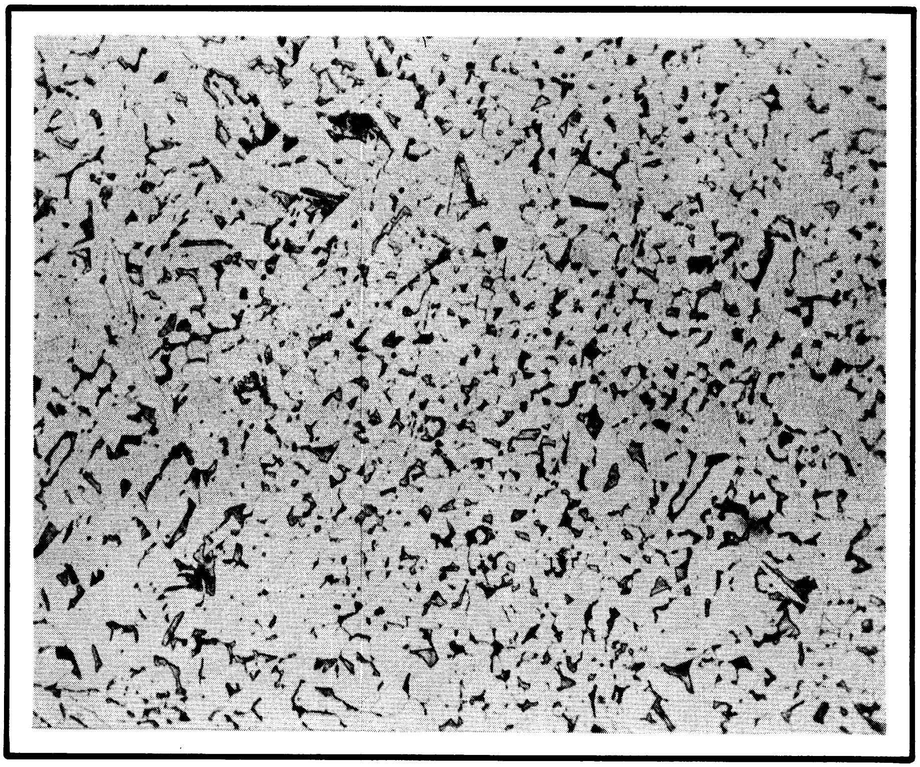


RELATION BETWEEN CREEP STRENGTH AND ACTIVE NITROGEN FOR VACUUM TREATED AND SPECIAL AIR MELTED STEELS

FIGURE 21



500 X

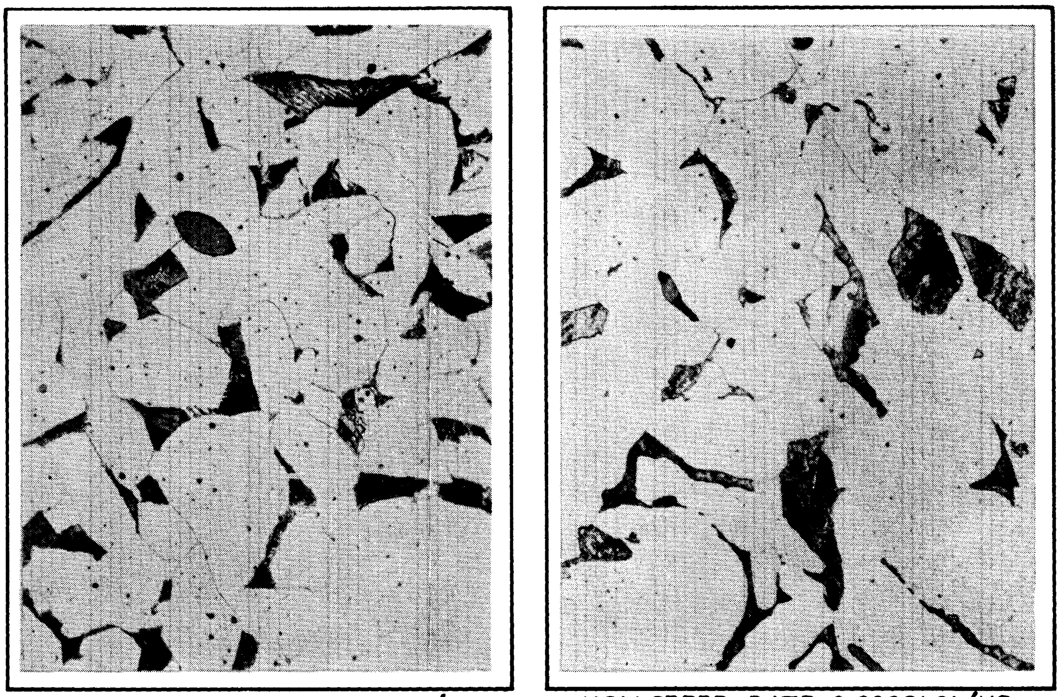


100 X

FIGURE 22: HEAT 1019, VACUUM MELTED STEEL, CREEP RATE 0.40 %/HR. NITAL ETCH.

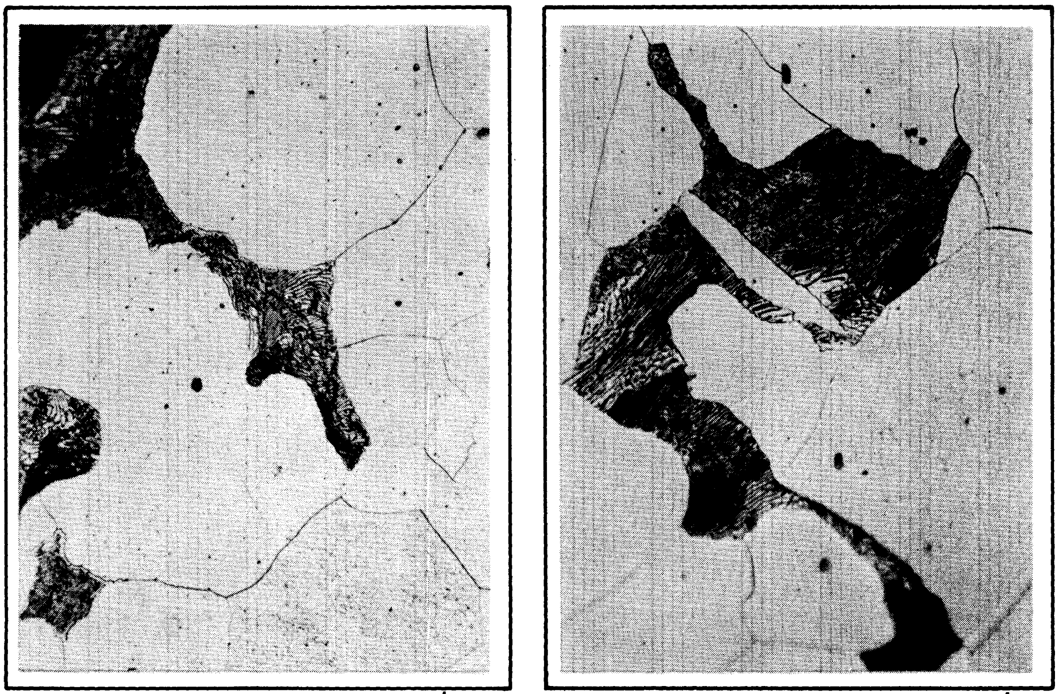
STEEL A
0.004 % NITROGEN

STEEL H
0.012 % NITROGEN



ACA: CREEP RATE 0.00022 %/HR.

HCA: CREEP RATE 0.00031 %/HR.



ACF: CREEP RATE 0.00046 %/HR.

HCF: CREEP RATE 0.000049 %/HR.

FIGURE 23: MICROSTRUCTURES OF RIMMED STEELS, NITAL ETCH, MAGNIFICATION 500 X.

APPENDIX

Calculation 1. -- Time required for removal of nitrogen from 0.252 inch bars by vacuum diffusion.

For diffusion, the variation of concentration with time is correlated by a ratio

$$\frac{Dt}{L}$$

Where: D = the diffusion rate
t = time in hours
L = thickness of the bar

The values for nitrogen extraction are:

t = 100 hrs.
$C = 40 \times 10^{-8}$ cm.^{2}/sec. at 2000° F
L = 1/4 inch

$$\frac{Dt}{L} = \frac{40 \times 10^{-8} \times 100 \times 3600}{0.252 \times 25.4} = 0.593$$

for $\frac{Dt}{L} = 0.593$; $\frac{Cm-Co}{Cs-Co} = 0.85$ for a round bar (42).

Where: Cm = mean final concentration
Co = mean original concentration = 0.004
Cs = surface concentration = 0.000

$$\frac{Cm - 0.004}{1 - 0.004} = 0.85$$

Cm = 0.0007% (calculated)
Cm = 0.0013 to 0.0016% (measured)

Calculation 2. -- True stress-true strain calculation for steel FCA at 400° F.

Formula

$$e_{tr} = \ln \frac{L}{Lo} = 2 \ln \frac{do}{d} \quad \ldots\ldots\ldots\ldots \quad (32)$$

where: e_{tr} is the true strain
L and Lo are the instantaneous and original measured length
d and do are the original and instantaneous diameters

L	ln L/Lo	True Strain e_{tr} in./in.	Area in.^{2}	Load lbs.	True Stress psi
2.995	0	0	.1995	50	250
2.9953	0.00010	0.00010	.1995	400	2,010
2.9955	0.00018	0.00018	.1995	1,000	5,020
2.9959	0.00030	0.00030	.1995	1,500	7,530
2.9962	0.00040	0.00040	.1995	2,000	10,050
2.9964	0.00048	0.00048	.1995	2,500	12,550
2.9968	0.00058	0.00058	.1994	3,000	15,050
2.9984	0.00112	0.00112	.1993	3,500	17,550
2.9985	0.00115	0.00115	.1993	4,000	20,100
2.9988	0.00127	0.00127	.1993	4,500	22,550
2.9990	0.00134	0.00134	.1992	5,000	25,100
2.9993	0.00144	0.00144	.1992	5,500	27,600
2.9998	0.00159	0.00159	.1992	6,000	30,100
3.0089	0.00464	0.00464	.1986	6,900	34,700
3.0315	0.01219	0.01211	.1971	9,000	45,700
3.0404	0.01516	0.01506	.1965	10,310	52,500
3.0667	0.02394	0.02366	.1948	11,690	60,100
3.0931	0.03275	0.03222	.1932	12,710	65,800
3.1066	0.03726	0.03658	.1923	13,090	68,100
3.1205	0.04190	0.04027	.1915	13,420	70,200
3.1487	0.05130	0.05005	.1898	13,880	73,200
3.1766	0.06063	0.05886	.1881	14,210	75,600
3.2059	0.07042	0.06805	.1864	14,420	77,400
3.2394	0.08160	0.07844	.1844	14,550	79,100
3.2683	0.09125	0.08732	.1829	14,610	79,900
3.2881	0.09786	0.09336	.1817	14,590	80,500 Max.
3.3054	0.10364	0.09861	.1808	14,530	80,500
3.3254	0.11032	0.10465	.1797	14,430	80,500
3.3415	0.11569	0.10947	.1788	14,280	80,000
3.3597	0.12177	0.11491	.1778	14,075	79,300
3.3784	0.12801	0.12054	.1768	13,820	78,200
.....	......	0.19492	.0901	11,980	133,100

Calculation 3.--Correlation (35) of dissolved nitrogen with logarithm of the creep rate for deoxidized steels.

Code	x Dissolved Nitrogen % x 10^4	y Log Creep Rate	$\sum x^2 - n(M_x)^2$	$\sum x$	$\sum xy - nM_xM_y$	$\sum y$	M_y	$\sum y^2 - n(M_y)^2$
BFA	8.0	-2.587	17356.50	551	-2177.445	-82.678	-3.445	304.387
BFF	9.0	-2.346	-12650.00		1898.149			-285.156
BCA	31.5	-4.411	4706.50		- 279.296			19.231
BCF	12.0	-2.400						
CFA	42.0	-4.529						
CFF	42.0	-4.826						
CCA	42.0	-4.604						
CCF	42.0	-4.484						
DFA	29.0	-4.563						
DFF	10.5	-2.563						
DCA	35.5	-4.182						
DCF	34.5	-3.679						
EFA	1.5	-2.339						
EFF	8.5	-2.611						
ECA	37.5	-4.303						
ECF	17.0	-2.532						
FFA	29.5	-3.099						
FFF	8.0	-2.631						
FCA	33.5	-4.303						
FCF	25.0	-2.980						
JFA	3.0	-2.542						
JFF	2.0	-2.491						
JCA	35.0	-4.163						
JCF	18.5	-3.510						

$$b = \frac{\sum xy - nM_xM_y}{\sum x^2 - n(M_x)^2}; \quad b = \frac{-279.296}{4706.50} = -0.0593$$

$$a = M_y - bM_x; \quad a = -3.445 + 1.362 = -2.083$$

log creep rate = -2.083 - 593 x % N

$$r = \frac{\sum xy - nM_xM_y}{\sqrt{\left[\sum x^2 - n(M_x)^2\right]\left[\sum y^2 - n(M_y^2)\right]}}; \quad r = \frac{279.296}{\sqrt{4706.5 \times 19.231}} = 0.927$$

$$r'^2 = 1 - 0.141 \times \frac{23}{22} = 0.852$$

$$r' = 0.923;\ \text{significant}$$

Calculation 4.--Correlation (35) of nitrogen with the logarithm of the creep rate for rimmed steels. (Assumption 0.0063 maximum effect.)

x % N x 10^4	y log creep rate
40.0	-3.678
40.0	-3.444
40.0	-3.658
40.0	-3.337
63.0	-4.027
63.0	-4.509
63.0	-4.310
13.5	-2.627

$\Sigma x^2 - n(M_x)^2$	Σx	$\Sigma xy - nM_xM_y$	Σy	M_y	$\Sigma y^2 - n(M_y)^2$
18489.25 -16425.78 2063.47	362.5	-1409.443 1340.797 - 68.646	-29.59	-3.699	111.930 -109.446 2.482

$$b = \frac{\Sigma xy - nM_xM_y}{\Sigma x^2 - n(M_x)^2} \; ; \; b = \frac{-68.646}{2063.47} = -0.0333$$

$$a = M_y - bM_x \; ; \; a = -3.699 + 1.524 = -2.175$$

log creep rate = -2.175 - 333 x % N

$$r = \frac{\Sigma xy - nM_xM_y}{\sqrt{\left[\Sigma x^2 - n(M_x)^2\right]\left[\Sigma y^2 - n(M_y)^2\right]}} \; ; \; r = \frac{68.646}{\sqrt{2063.47 \times 2.482}} = 0.9588$$

$$r'^2 = 1 - 0.0412^2 \times \frac{7}{6} = 0.952$$

r' = 0.976, significant

Calculation 5.--Correlation of manganese with creep rate for steels with 0.001 to 0.002 percent nitrogen.

Code	x Mn % x 10^2	y Log Creep Rate	$\sum x^2 - n(M_x)^2$	$\sum x$	$\sum xy - nM_xM_y$	$\sum y$	M_y	$\sum y^2 - n(M_y)^2$
BCF	43	-2.400	32825 -21889 10936	573	-1551.871 1182.290 - 369.581	-30.941	-2.063	78.3233 -63.8602 14.4631
DFF	42	-2.563						
ECF	43	-2.532						
JCF	82	-3.510						
FCS	68	-2.346						
FFS	68	-2.688						
CFX	68	-3.222						
CCF	68	-3.432						
19FA	5	-0.389						
19CA	5	-0.679						
79FA	1	-0.658						
18FA	25	-1.377						
18CA	25	-2.199						
42FA	29	-1.827						
16CA	1	-1.119						

$$b = \frac{\sum xy - nM_xM_y}{\sum x^2 - n(M_x)^2} \; ; \; b = \frac{-369.581}{10936} = -0.033795$$

$$a = M_y - bM_x \; ; \; a = -2.063 + 1.291 = -0.772$$

log creep rate = -0.772 - 33.8 x % Mn

$$r = \frac{\sum xy - n \quad M_yM_x}{\sqrt{\left[\sum x^2 - n(M_x)^2\right]\left[\sum y^2 - n(M_y)^2\right]}} \; ; \; r = \frac{369.581}{\sqrt{(10936) \times 14.463}}$$

$$r'^2 = 1 - 0.137 \times \frac{14}{13} = 0.8125$$

$r' = 0.901$, significant

Calculation 6.--Difference between actual and calculated creep rates.

Code	log $\dot{E}$ Calculated	log $\dot{E}$ Actual	Actual - Calc. Difference x 10^3
BFA	-2.557	-2.587	- 30
BFF	-2.617	-2.346	271
BCA	-3.951	-4.411	-460
BCF	-2.995	-2.400	395
CFA	-4.583	-4.529	54
CFF	-4.583	-4.826	-243
CCA	-4.583	-4.604	- 21
CCF	-4.583	-4.484	99
DFA	-3.803	-4.563	-760
DFF	-2.706	-2.563	143
DCA	-4.188	-4.182	6
DCF	-4.129	-3.679	450
EFA	-2.172	-2.339	-167
EFF	-2.587	-2.611	- 24
ECA	-3.951	-4.303	-352
ECF	-3.091	-2.532	559
FFA	-3.832	-3.099	734
FFF	-2.557	-2.631	- 74
FCA	-4.070	-4.303	-233
FCF	-3.566	-2.980	586
JFA	-2.261	-2.542	-281
JFF	-2.202	-2.491	-289
JCA	-4.159	-4.163	- 4
JCF	-3.180	-3.510	-330

Calculation 7.--Analysis of variance (36) of the effect of heat-treatment and steel on the variation from the correlation curves for steels "B", "D", and "E" (0.43 Mn) and all deoxidized steels.

Item	Sum of Squares	Degrees Freedom	Mean Square	F Ratio	Significance
0.43 Manganese Steels					
Between Heat-Treatment	410,155	3	136,718	0.61	None
Between Deoxidation	56,383	2	28,191	0.13	None
Residual	1,342,637	6	223,773	....	....
Total	1,709,175	11	......	....	....
All Deoxidized Steels					
Between Heat-Treatment	497,696	3	165,899	1.05	None
Between Steels	119,480	5	23,896	0.15	None
Residual	2,374,661	15	158,311	....	....
Total	2,994,737	23	......	....	....

Conclusion: Neither heat-treatment nor type of deoxidation causes any significant variation from the correlation curve.

Calculation 8.--Correlation (35) of the deviation of the individual tests from correlation curve in Figure 2 with hardness.

x Hardness Rockwell B	y Log $\dot{E}$	$\sum x^2 - n(M_x)^2$	$\sum x$	$\sum xy - nM_xM_y$	$\sum y$	M_y	$\sum y^2 - n(M_y)^2$
65.0	-0.030	98704.00 -95382.04 3321.96	1513.0	-23.5060 - 1.1347 -24.6408	+0.018	+0.0075	2.431
57.5	+0.271						
63.5	-0.462						
52.0	+0.395						
75.0	+0.054						
68.0	-0.252						
75.5	-0.021						
69.0	+0.099						
55.0	-0.760						
41.5	+0.143						
57.5	+0.006						
38.0	+0.450						
57.0	-0.167						
53.0	-0.024						
58.0	-0.352						
40.0	+0.559						
75.5	+0.734						
74.0	-0.074						
74.5	-0.233						
68.0	+0.586						
75.0	-0.281						
71.0	-0.289						
77.5	-0.004						
72.0	-0.330						

$$b = \frac{\sum xy - nM_xM_y}{\sum x^2 - n(M_x)^2} \; ; \quad b = \frac{-24.6408}{3321.96} = -0.0074175$$

$$a = M_y - b\,M_x \; ; \quad a = 0.4676 + 0.0075 = 0.4761$$

log creep rate = 0.476 -0.007 x hdns.

$$r = \frac{\sum xy - nM_xM_y}{\sqrt{\left[\sum x^2 - n(M_x)^2\right]\left[\sum y^2 - n(M_y)^2\right]}} \; ; \quad r = \frac{-24.6408}{\sqrt{97.185}} = 0.2535$$

$p = > 0.10$, not significant

(37) Calculation 9.--Segregation of nitrogen in rimmed steels and test for difference between rim and core.

$$t = \frac{\overline{x} - \overline{y}}{S}\sqrt{\frac{nm}{n + m}} \qquad (n + m - 2) \text{ degrees freedom}$$

$$S = \frac{x_i^2 - (x_i^2)/n + y_i^2 - (y_i)^2/n}{(n + m - 2)}$$

$$S = \frac{\overset{(33.74)}{25 + 8.74}}{53} = 0.636$$

$$t = \frac{\overset{(1.22)}{2.74 - 1.52}}{\sqrt{6.36}} \sqrt{\frac{28 \times 27}{55}} = 5.67 \qquad \text{d.f.} = 53$$

for the 0.001 level, $t = 4.523$

therefore $p = < 0.001$

Conclusion: There is significantly more nitrogen in the core material than the rim for a rimmed low carbon steel ingot.

Calculation 10.--Calculation of maximum nitrogen in terms of nitrogen associated with dislocations.

Assume 0.0063 nitrogen maximum effect (from test data)

$$\frac{0.0063 \text{ gm N}/14}{100 \text{ gm Fe}/58} = \frac{0.00045}{1.7921} = .025 \text{ Atomic } \%$$

$$\frac{2.5 \text{ N}}{10{,}000 \text{ atoms Fe}} = \frac{2 \text{ atoms N}}{8 \times 10^3 \text{ atoms Fe}}$$

$$1 \text{ cm}^2 \text{ metal} \times \left(\frac{1 \text{ atom}}{2.861 \times 10^{-8} \text{ cm}}\right)^2 = \frac{1 \text{ atom Fe}}{1.23 \times 10^{-15} \text{ cm}^2}$$

Take a section 1 cm^2 by 1 atom

$$\frac{1}{1.23 \times 10^{-15}} \times \frac{2}{8 \times 10^3} = 2.03 \times 10^{11} \text{ atoms N/cm}^2$$

There are from 10^8 to 10^{12} dislocations per cm^2. (41)

This is of the same order as the number of atoms of nitrogen/cm^2 assuming 1 atom of nitrogen per dislocation.

If the dislocations' average length is 500 A (the width of a slip plane) and it is assumed that nitrogen must form an atmosphere along the complete length:

$$\frac{2.03 \times 10^{11}}{200} = 1 \times 10^9 \text{ atmospheres/cm}^2$$

which is still of the same order as the dislocations.

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