UNIVERSITY OF CINCINNATI

May 22 1946

I hereby recommend that the thesis prepared under my supervision by Ele Eugene Stansbury

entitled A Study of Several variables affecting the Rate of Martensite Formation

be accepted as fulfilling this part of the requirements for the degree of Doctor of Philosophy.

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Form 668—G. S. and Ed.—1M—7-37

A STUDY OF SEVERAL VARIABLES
AFFECTING THE
RATE OF MARTENSITE FORMATION

A dissertation submitted to the

Graduate School of Arts and Sciences
of the University of Cincinnati

in partial fulfillment of the
requirements for the degree of

DOCTOR OF PHILOSOPHY

1946

by

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Acknowledgement

The author wishes to acknowledge the many helpful suggestions of the various members of the Chemical and Metallurgical Engineering Staff. In particular he wishes to express his appreciation for the continued encouragement and many suggestions given him by Professor John F. Kahles, Dr. R. O. McDuffie, and Professor R. S. Tour.

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INTRODUCTION

The tremendous number of investigations that have been made on the decomposition of austenite during the last fifteen years is ample evidence of the importance of this study in the field of metallurgical research (1)(2)(3). Much of the data obtained from these investigations has been presented in the form of "so-called" S-curves or more properly in the form of time-temperature-transformations curves since the characteristic "S" shape is retained only in the plain carbon and low alloy steels. The systematic examination of the data presented by these curves has done much to explain previously observed facts and has stimulated both theoretical and practical research in the field of thermal treatment of iron and steel. Today there are many commercial heat treating processes which have been developed as a result of these studies.

The work of a number of investigators (4)(5)(6) prior to 1930 had shown that there were times of apparent inactivity before the austenite of a given steel would start to transform and that the extent of this so-called "lag-time" depended on the number of degrees of cooling below the lower critical temperature of the steel. In 1930 Davenport and Bain (7) published the results of an extensive investigation on the isothermal decomposition of austenite at various temperatures between the lower critical temperature and room temperature. Although it was later shown (8)(9)(10) that some of their data were incorrect due to the experimental method used, the general picture of austenite decomposition which they presented may be considered as the initial outstanding contribution in this field. They showed that at temperatures just below the lower critical temperature the lag-times before the start of transformation were rather long decreasing to a minimum between 500°C and 600°C. In this minimum range, the transformation would start in anywhere from less than one up to about ten seconds for the plain carbon steels, the exact time depending upon the carbon content of the steel and the initial grain size of the austenite. Below this range of temperature, the lag-times again increased reaching a maximum around 300°C. The graph of these data when plotting temperature against lag-time frequently resembles the letter "S", hence the term S-curve. The results which they obtained at lower temperatures will be discussed in connection with the investigations on martensite formation.

The work of Davenport and Bain stimulated considerable interest and activity in the study of austenite decomposition in both the plain carbon and the alloy steels. A number of the more important contributions are listed in the bibliography included at the end of this dissertation. (1)(2)(3)(8)(11) The paper by Davenport published in 1939 is of special importance. (11)

Practically all of the work that has been done up to the present time has dealt with the isothermal decomposition of austenite at various temperatures below the lower critical temperature. This method of attack on the problem has been necessitated because of the difficulties involved in obtaining reliable data when the two variables, time and temperature, are varied at the same time. That such experimental difficulties do arise is unfortunate, since most heat treating processes are carried out under conditions in which the time and temperature are both changing, i.e., on continuous cooling. In some cases however continuous cooling diagrams have been determined. Grange and Kiefer (12) studied the continuous cooling decomposition of SAE 4340 and developed an empirical method for determining the continuous cooling diagram from the isothermal one. Liedholm (13) has developed a method for determining the continuous cooling diagram by a modified end quench method. The products obtained from the decomposition of austenite on continuous cooling, providing the rate of cooling is not too fast, are mixtures of those obtained by isothermal decomposition. The type of product obtained at any instant during continous cooling will be similar to the product obtained by isothermal transformation at that temperature.

When the rate of cooling is increased until the formation of the higher temperature products is prevented, the nature of the decomposition product changes materially from the ones previously obtained. The product which is known as martensite is more homogeneous, harder and possesses entirely different etching characteristics. The only instances in which martensite will not be obtained under conditions of very rapid cooling are those in which austenitic stainless steels or high carbon-high alloy steels are quenched. In these latter cases, the austenite formed at temperatures above the critical temperature will remain as such at room temperature. Continued cooling to subatmospheric temperatures may or may not allow the formation of martensite in these steels.

Due to the experimental procedure employed by Davenport and Bain (7) and by Davenport (11) and others, it was reported that the formation of martensite was proceeded by a lag-time similar to the lag-times found prior to the formation of the various products at higher temperatures. This time interval decreased rapidly as the decomposition was allowed to occur progressively lower in the range of martensite formation. At the lower temperatures they reported time intervals smaller than could be detected experimentally. In 1940 Greninger and Troiano (10) proved that there was no lag-time prior to the formation of martensite, that martensite was a product of continuous cooling, and that if cooling were interrupted the process of martensite formation would stop until the cooling was continued. This mode of formation of martensite was further substantiated by the work of Saunders and Kahles (9) and by additional work by Greninger (10) in which cooling rates as high as 12,000°C per second were not sufficient to repress the formation of martensite at a temperature fixed for a given steel. These latter investigations have substantiated the earlier theory of Robertson (14) that martensite was a product of cooling and not one formed at constant temperature.

In general, therefore, it may be stated that the austenite of a given steel may decompose into either of two types of transformation products. The first type of product (of which there may be several variations) results from the transformation of austenite isothermally in the temperature range between the lower critical temperature and the temperature of martensite formation, i.e., the M_s temperature. The second type of product, martensite, results from the transformation of austenite on continuous cooling below a definite temperature, the M_s temperature, and continues to form only as cooling continues until the transformation is complete at the M_f temperature. Although martensite forms on continuous cooling, the untransformed portion of the austenite will isothermally decompose if held for a sufficient length of time at some temperature between the M_s and M_f temperatures. The product of this decomposition is not of the same nature as the martensite but rather has the characteristics of the type of product obtained through isothermal transformation above the M_s temperature.

It is convenient to plot both the isothermal transformation data and the continuous cooling martensite data on the same graph, plotting time on a log scale against the temperature. Since some of the earlier charts or S-curves were referred to as isothermal transformation diagrams, there might be some inconsistancy in including the martensite data. In order to avoid any confusion from this point, the use of the term time-temperature-transformation diagram is to be recommended realizing that two fundamentally different types of transformations are involved.

It has been stated that in order for a given amount of austenite to completely transform into martensite it is necessary that the rate of cooling down to the M_s temperature be rapid enough to prevent transformation into any of the products capable of formation at higher temperatures. The cooling rate which will just allow this to be accomplished is referred to as the critical cooling velocity. In order to produce full martensitic hardening in any steel it is necessary to equal or exceed this critical cooling velocity. The two most important variables governing the value of the critical cooling velocity are the composition of the steel and its austenitic grain size.

Assuming that this critical cooling velocity can be exceeded there are then a number of variables which can affect the temperature at which martensite will begin to form and the progress of its transformation as the temperature is decreased. Closely related to the formation of martensite is the problem of the isothermal transformation of the untransformed austenite existing below the M_s temperature. There have been a number of investigations carried out on the effect of several variables on these transformations. Most of the work has been carried out with the medium and high alloy steels where the reaction rates are slower and consequently may be studied more easily. Furthermore, the M_f temperatures for many of these steels are below room temperatures which allows the study of the effects of retained austenite at room temperature.

Few systematic studies have been made on the variables affecting the course of transformation in the lower temperatures for the plain carbon steels. Since these steels form the basis upon which the alloy steels are built, it was thought that it would be of fundamental importance to investigate some of these variables. The following dissertation discusses in more detail the nature of the transformations occuring in the lower temperature ranges, the importance of the several variables considered, and the effects of the variables on the transformations.

THEORY OF AUSTENITE-BAINITE AND AUSTENITE-MARTENSITE TRANSFORMATIONS

In any phase transformation such as those which occur when austenite decomposes into various products, there are three fundamental questions to be answered. In the first place it is necessary to show thermodynamically that the phase change will occur. In the second place it is desirable to produce a mechanism by which the change may be brought about. Finally, the rate of transformation and the variables affecting the rate is important. For the decomposition of austenite these questions have been answered to varying degrees of accuracy. The work that has been done on the first two of these problems will be briefly discussed in view of recent investigations. The third item will be discussed in relation to the results of this investigation.

Zener (15) has recently considered the entire problem of the decomposition of austenite at all temperatures below the critical temperature using the methods of thermodynamics and statistical mechanics. Through these methods he has been able to show that there are three types of decomposition processes, two being very much different and the third similar in some respects to each of the others. The following discussion is mostly based on Zener's paper with the exception of some change in nomenclature. Since the experimental work reported in this dissertation was confined entirely to the transformation of austenite into martensite and bainite, most of the discussion will be restricted to these topics.

In the temperature range just below the lower critical temperature, the products of decomposition have the characteristics of the equilibrium products, i.e., alpha ferrite and iron carbide or cementite. The transformation begins after a definite lag time and progresses to completion through a process of nucleation and growth,the final products being lamellar in character and composed of alpha ferrite and cementite, i.e., pearlite. The rate at which a pearlite nuclei grows is directly proportional to the diffusion coefficient of the carbon in the austenite and to the respective difference in carbon concentration of the austenite in front of the advancing ferrite and cementite plates. The rate is inversely proportional to the interlamellar spacing of the pearlite. The difference in carbon concentration is greater and the interlamellar spacing is smaller the greater the amount of under-cooling. When the temperature is on the high side of this range, the time lag before the beginning of transformation is long because of the slow rate of nuclei formation even though the rate of diffusion is high. At lower temperatures, on the other hand, the rate of nuclei formation is high but the rate of diffusion is sufficiently smaller to make the lag time long. Only at intermediate temperatures (600°C to 650°C) will the various factors allow transformation to start in a relative short time. This range in which the lag times are small locates the so-called "nose" of the "S" and on continuous cooling, that rate which just prevents transformation at this point establishes the critical cooling velocity of the steel.

The necessary condition for a phase change to occur is that there be a decrease in the free energy of the system as the transformation takes place. It may be possible that several phase changes occur with a different decrease in free energy. The one that does take place is the one having the fastest rate of reaction even though others may occur with greater decreases of free energy. In the transformation of austenite to pearlite it has been stated that because of the low rate of diffusion of carbon as the temperature is lowered, the time for the beginning of transformation becomes extremely long. Since the formation of pearlite requires diffusion of carbon over relatively large distances, other phase changes tend to occur at the lower temperatures because the rate of transformation becomes greater than the rate of pearlite formation. With reference to the decomposition of austenite, products tend to form with the same composition as the original austenite i.e., the face centered cubic austenite tends to change to body centered cubic without the normal rejection of carbon.

For the transfer of one mol of iron containing X mols of carbon from austenite to ferrite of the same composition the change of free energy is given by:

$$\Delta F = \Delta F_{Fe}^{\gamma\to\alpha} + X\Delta F_{c}^{\gamma\to\alpha} - XT\Delta S_{c}^{\gamma\to\alpha} \qquad (1)$$

where $\Delta F_{Fe}^{\gamma\to\alpha}$ is the change of free energy when gamma iron is transformed into alpha iron at temperature T, $\Delta F_{c}^{\gamma\to\alpha}$ is the change in free energy for the transfer of one mole of carbon from austenite to ferrite and $\Delta S_{c}^{\gamma\to\alpha}$ is the change of entropy per mol of carbon. When ΔF is set equal to zero a relation is obtained between the concentration and the temperature at which austenite will change into ferrite of the same carbon concentration. Zener points out that there is some question as to whether the change in entropy should be considered, and concludes that it should in cases where the transformation is slow.

When considering the formation of martensite and the lower forms of bainite, it will be assumed that the change in entropy of the carbon atoms may be neglected. On this basis, the above equation reduces to

$$X\Delta F_{c}^{\gamma\to\alpha} = -\Delta F_{Fe}^{\gamma\to\alpha}$$

The free energy change for transfer of one mol of carbon from the gamma phase to the alpha phase is computed from the following equation for the equilibrium between two phases (24).

$$\frac{C_j^{\alpha}}{C_j^{\gamma}} = \beta_j e^{-\frac{\Delta F}{RT}}$$

Where C_j^{γ} and C_j^{α} = mol fractions of the jth components in the two phases

R = gas constant, cal/degree abs.

T = temperature, degrees abs.

β_j = Weight factor equal to 1 for substitutional type solid solutions and 3 for interstitial type solid solutions in which ratio of interstitial positions to lattice positions is 3, i.e., α -iron.

ΔF = heat absorbed when one mol of dissolved element is transferred from the gamma to alpha phase.

For a plain carbon steel the relation becomes:

$$\frac{C_c^{\alpha}}{C_c^{\gamma}} = 3e^{-\frac{\Delta F_c}{RT}}$$

At 723°C, C_c^{α} equals 0.045% carbon and C_c^{γ} equals 0.83% carbon. Substitution of these values for the carbon concentrations, a value of 8,100 cal/mol is obtained for ΔF_c. The value of this energy change varies somewhat with the temperature but in view of the fact that the results can only be calculated semiquantitatively anyhow, taking it as constant at 8,100 cal/mol will not materially change the results. There then results

$$\Delta F_c^{\gamma \rightarrow \alpha} = -8,100\ X_c \qquad (2)$$

The temperature at which the change from the gamma phase to the alpha phase occurs with a decrease in free energy satisfying the above equation for a given carbon content will be the critical temperature for the transformation. To evaluate the free energy change it is necessary to consider the thermal data for the two phases and compute the free energy as a function of the temperature.

From $F = H - TS$

get
$$dF = dH - TdS - SdT$$
$$= dE + pdv + vdp - TdS - SdT$$
$$= vdp - SdT$$

where F is the free energy in calories per mol, H the enthalpy in calories per mol, T the absolute temperature, S the entropy in calories per mol per degree abs., E the internal energy per mol, and pdv and vdp the molar pressure volume products expressed in calories.

At constant pressure $dF = -SdT$

For a change of state at constant pressure

$$d\Delta F = -\Delta SdT$$

Therefore

$$\Delta F_{Fe} = -\int_{T_o}^{T} \Delta S_{Fe} dT$$

where T_o is the equilibrium transformation temperature.

If L equals the latent heat of the transformation, then

$$\Delta S = -\frac{L}{T_o} - \int_{T_o}^{T'} \frac{\Delta C_{Fe}}{T''} dT''$$

therefore

$$\Delta F_{Fe} = -\int_{T_o}^{T} \left[-\frac{L}{T_o} - \int_{T_o}^{T'} \frac{\Delta C_{Fe}}{T''} dT'' \right] dT'$$

$$= -L\frac{(T_o-T)}{T_o} + \int_{T_o}^{T}\int_{T_o}^{T'} \frac{\Delta C_{Fe}}{T''} dT''dT'$$

where ΔC_{Fe} = specific heat of α phase - specific heat of γ phase.

Zener (14) has evaluated this double integral from the specific heat data of Austin (16) on the alpha and gamma forms of iron and has given a table for the values of $\Delta F^{\gamma \to \alpha}$ as a function of the temperature. In this matter it is possible to theoretically compute the temperatures at which austenite of various contents should begin to transform into ferrite of the same carbon content.

The products formed under the above conditions are known as bainite and the range of formation of this product relative to the other transformations products is given in Fig. 1 for an arbitrary carbon content. It is seen that the curves representing the various amounts of transformation are somewhat similar to those for the formation of pearlite except for the fact that the upper portions of the curves are horizontal and that the isothermal transformation stops after a certain amount of time has elapsed. There are at least theoretical explanations for these characteristics. The computations above have shown that in order for any bainite to form it is necessary that transformation occur below a certain critical temperature. Assuming that the temperature of a given amount of austenite has been lowered below this critical value, a certain time is required for the first nuclei of high carbon ferrite to form. Once the nuclei have formed they will grow to a certain extent and then stop as shown by the series of horizontal lines. There are two possible explanations for this occurance. In the first place even though the formation of bainite does not require the diffusion of carbon through the austenite, carbon can rapidly diffuse through the supersaturated ferrite out to the surrounding austenite. The diffusion rates of carbon in ferrite are known to be high and are probably due to the greater number of adjoining interstitial positions in the alpha phase than in the gamma phase. This increase in the carbon content of the austenite in contact with the bainite may lower the critical temperature for the formation of additional amounts of bainite to a temperature below that at which transformation is occurring thus preventing further transformation.

In the second place, the high carbon concentration may cause the formation of a continuous film of cementite around the bainite and thus stop its further transformation. In either case, at lower temperatures the rate of diffusion of carbon in the ferrite is so low that the carbon content of the remaining austenite is not changed and the transformation may go to completion. It is also found that the lag time before the beginning of transformation is lower the lower the temperature and the transformation characteristics in this respect become more similar to the "C" curves of pearlite formation. The separation of the pearlite transformation from the bainite transformation is observable only in the high alloy steels (18). For medium alloy and plain carbon steels, the two types of transformations are not individually distinguishable.

If a given amount of austenite is cooled at a sufficiently high rate so as to prevent the formation of either pearlite or bainite, a temperature is reached at which transformation starts on continuous cooling. The product which starts to form is known as martensite and is similar to bainite in that no diffusion of carbon in the austenite is involved but is different in that the carbon atoms seem to assume preferred interstitial positions in the transformation structure. As a consequence, the resulting space lattice is elastically strained into a body centered tetragonal structure with the preferred interstitial positions parallel to the tetragonal axis.

Barrett (17) reports that the period of time required for the formation of a given amount of martensite is less than 0.002 seconds. As a consequence of the requirement that a highly elastically strained lattice must form almost instantly, an additional energy term must be added to the free energy equation 1. Denoting this strain energy by ΔE the relation becomes

$$\Delta F^{\gamma\rightarrow\alpha} = \Delta F_{Fe}^{\gamma\rightarrow\alpha} + X\Delta F_{c}^{\gamma\rightarrow\alpha} - XT\Delta S^{\gamma\rightarrow\alpha} + \Delta E$$

Since the transformation occurs so rapidly and at such low temperatures it is reasonable that the carbon atoms do not undergo a change in entropy. As a result of this additional eneggy term, the temperature at which the transformation starts is lowered about 250°C below that computed for the start of bainite formation in the case of no entropy change for the carbon atoms.

An estimate of the magnitude of this strain may be made by taking the experimentally determined temperatures for the beginning of martensite formation and solving for the strain energy. Referring back to equation 2 it is seen that for a 0.83 % carbon steel, ΔF_{Fe} must be equal -390 cal. Reference to Zener's tables gives a temperature of about 465°C. This would be the temperature for the beginning of transformation to bainite neglecting the entropy change for the carbon atoms. The experimental M_s point for a 0.83% carbon steel is about 250°C. This corresponds to ΔF_{Fe} equal to 690 cal. The difference between these two values corresponds to the strain energy and is seen to be about 300 cal.

Various investigations (7)(8)(9) have shown that martensite forms on continuous cooling and if the cooling is stopped within the M_s - M_f range, the martensite will cease to form until the cooling is again continued. From the above theory it would seem logical to state that each increment of martensite that is formed increases the strain energy ΔE required for further transformation. Thus the formation of additional amounts of martensite will arise only through the lowering of the temperature. If the temperature is held constant after a certain amount of martensite has formed, then isothermal transformation of the remaining austenite will start after a definite period of time, the product being bainite.

The above discussion has presented from a thermodynamical standpoint the conditions under which it is possible for austenite to transform into the various types of decomposition products. Only in certain cases has the mechanism whereby the transformations may occur been mentioned. In the case of pearlite formation it seems rather definite that the transformation occurs through a process of nucleation and growth and that considerable diffusion of carbon in the austenite is necessary to bring about the transformation. Whereas a partially satisfactory theory for the nucleation and growth has been worked out for pearlite formation (15), no such theory has as yet been developed for the formation of bainite. Nevertheless it seems probable that bainite forms through a process of nucleation and growth of ferrite of the same carbon content as the austenite from which it is transforming. When the temperature is sufficiently high, the formation of the supersaturated ferrite is probably followed by diffusion of carbon and precipitation of some type of iron carbide.

When martensite forms from austenite there is no lag time prior to transformation and hence no nucleation and growth at least of the same nature as for the bainite formation. The results of a number of investigations would seem to show that martensite forms thorough some type of shear converting a definite section of the austenite into martensite in a very short period of time. Barrett (17) has reviewed the work of Kurdjumow and Sachs (14), Nishiyami (2), Wassermann(21) and Mehl and Derge (22). Kurdjumow and Sachs prepared large grained austenite in a 1.4% carbon steel by slow cooling from the melt. After quenching in water enough austenite was retained to allow the relationship between the austenite and martensite lattices to be determined. They reported the following relationship

$$(111)_\gamma \parallel (\bar{1}10)_\alpha$$
$$(110)_\gamma \parallel (\bar{1}11)_\alpha$$

Nishiyami determined the austenite-martensite relationships in a 30% nickel iron-nickel alloy and arrived at the following

$$(111)_\gamma \parallel (110)_\alpha$$
$$(\bar{2}11)_\gamma \parallel (\bar{1}10)_\alpha$$

Mehl and Derge determined the lattice relationships of iron-nickel alloys of about the same nickel content and found that the Kurdjomow-Sachs relationship held when the transformation occured at high temperatures and that the Nishiyami relationship held at lower temperatures of transformation. It is possible to propose a mechanism whereby a given amount of austenite can be converted into martensite and give the above lattice relationships. It would be necessary for shear to occur on a slip plane of the austenite, (111) in the ($\bar{2}11$) direction followed by certain expansions and contractions which would produce the correct martensite lattice.

Greninger and Troiano (23) investigated the same problem in any alloy containing 22% nickel and 0.80% carbon. Their results for the lattice relationships between the austenite and martensite were very close to those given above but they concluded that the above mechanism was not without objection because of "the relatively large movement and re-adjustment required." In working out a more logical mechanism they developed a new method of attack on the problem, the stereographic analysis of shear. By this method they analyzed the relief effect produced on a polished surface of austenite after a portion of it had transformed into martensite and concluded that the transformation was some type of homogeneous shear. Whereas a close-packed hexagonal lattice can be converted into a face centered cubic structure by a single homogeneous shear, no single shear mechanism can convert the face centered cubic into a body centered cubic or tetragonal structure. They were able to show however that the transformation could be accounted for by considering two homogeneous shears with a slight adjustment after the first shear. There mechanism involves a first homogeneous shear on a plane of high indices in the austenite resulting in a special triclinic lattice. After a slight readjustment a second shear converts the triclinic lattice into a body centered lattice with an axial ratio greater than one. The continuation of the transformation into a body cubic centered lattice is prevented by the presence of the carbon atoms. According to Zener (15) the carbon atoms would be located in the interstitial positions parallel to the tetragonal axis.

DISCUSSION OF THE VARIABLES AND THEIR IMPORTANCE

In the previous section the conditions under which martensite forms and the mechanism whereby the transformation takes place has been discussed from both a theoretical and experimental standpoint. Relatively few quantitative studies have been made on the various factors that might affect the temperature at which the austenite-martensite transformation occurs and on the factors affecting the progress of transformation below the M_s temperature. There is also a lack of information on the rate of bainite formation both above and below the M_s temperature and on the effect of this bainite on the martensite formation. Of the investigations that have been made, few of them have been made on the plain carbon steels. The general lack of data is probably due to the difficulty of obtaining reproducible quantitative results. It has been difficult to duplicate samples and most of the methods for quantitatively determining the amounts of transformation are tedious and slow. That fewer investigations have been made on the plain carbon steels may be attributed to the greater speed with which transformations occur in the absence of alloying elements and to the fact that most plain carbon steels contain no retained austenite at room temperature. It is with respect to this retained austenite that many of the investigations on alloy steels have been made.

The effects of a number of variables on the formation of martensite were considered in the experimental work reported in this dissertation. Each of these variables will be discussed relative to the importance of the variables as such and its importance to investigations of a similar nature that have already been made.

1. The Effect of Austenitizing Temperature on the M_s Temperature and the Rate of Martensite Formation Below the M_s Temperature.

In considering the effect of the temperature of the austenite prior to quenching on the formation of martensite, it must be realized that two variables may be involved. In the first place there is the effect of the temperature as such and in the second place the higher austenitizing temperatures will produce larger austenitic grains which in turn may have their effect as such. For large grained austenite any final quenching temperature may be used by establishing the large grain size at high temperatures and then lowering the temperature for quenching. On the other hand even so-called fine grained steels will not assure a fine grained austenite over any great range of temperatures. The quenching of a fine grained austenite from a high temperature is impossible.

Considering that homogeneous austenite can be obtained at any of a series of temperatures, it would seem that the only effect of the temperature would be to impose different amounts of stress on the steel being quenched due to the greater thermal shock on quenching from the higher temperature. If the theoretical calculations of Zener are correct, i.e., the strain energy equals 300 calories per mol, it would require quenching stresses of the order of 1,500,000 pounds per square inch before they would effect the martensite formation. The relation between the strain energy expressed in calories per mol and in terms of stress in pounds per square inch may be derived through a consideration of the change in volume occuring when a mol of martensite is converted into ferrite, and cementite. An exact interpretation of such a relation is not possible. In the first place the stress distribution is difficult to evaluate and, in the second place, the absolute value and meaning of the strain energy is difficult to state. In either case it seems probable that very high stresses are involved in the actual formation of martensite and that the effect of thermal stress would be small in comparison to such transformation stresses.

If the effect of the austenitizing temperature as such can be considered as negligible, then the effect of quenching from higher temperatures would be that of quenching austenite of larger grain size. Theoretically it is difficult to predict the effect of grain size on the transformation of austenite to martensite. When it is considered that martensite forms through some type of homogeneous shear apparently unnucleated by the grain boundaries, the grain size should have no effect on the transformation. On the other hand the relief produced on the polished surface of a grain of austenite when a section of it transforms to martensite is an indication of the degree of shear which does occur. If this shear were interrupted by the grain boundaries or the overall expansion restricted by the surrounding grains then smaller grained austenite should transform more slowly than coarse grained material.

Very little quantitative information is available on the effects of the austenitizing temperature on the transformation of austenite to martensite. There have been numerous investigations (25)(26)(27) on the effect of the austenitizing temperature on the M_s temperature and on the amount of retained austenite at room temperature in the case of higher alloyed-high carbon steels. In most of these cases the changes of temperatures caused an increase or decrease in the amount of undissolved carbide present and thus a change in both the alloy and carbon content of the austenite. Austenite having such changes in composition has been shown to have different M_s and M_f temperatures.

Greninger (10) has reported some results of the effect of austenitizing temperature on martensite formation in the plain carbon steels. On increasing the austenitizing temperature of an eutectoid steel from 800°C to 1000°C the M_s temperature was raised by about 15°C. Also below the M_s temperature the rate of martensite formation was slower when using the higher quenching temperature. As a result the M_f temperature for the high quenching temperature was actually lower than when the steel was quenched from the lower temperature.

2. Effect of Martensite on the Formation of Bainite Below the M_s Temperature.

A number of early investigations (8)(9)(28) on the formation of martensite had indicated that there was a second reaction superimposed upon the martensite.

It was pointed out in the introduction that early investigators thought that martensite formed at a given temperature only after a definite lag time. With this picture of the transformation, they proceeded to get data showing that a second reaction started after the martensite. It was later shown that the martensite formed on continuous cooling and without any lag time. The second reaction which they encountered was no doubt the formation of bainite from the untransformed austenite. When Greninger and Troiano (8) proved that martensite formed directly on cooling to a temperature below that which is now referred to as the M_s temperature, they also presented some data on the beginning of bainite formation in this temperature range. Their results were only qualitative but indicated that the untransformed austenite would transform to bainite isothermally below the M_s point and that the lower the temperature the longer the time before the isothermal transformation started. Later Saunders and Kahles (9) studied the transformations occuring in the martensite range and showed more quantitatively that the untransformed austenite at any temperature did transform progressively to bainite and that the beginning of the transformation occured after longer time the lower the temperature. Some of their results seemed to indicate that the martensite just below the M_s temperature promoted the initial formation of bainite in shorter periods of time than when the bainite formed just above this temperature.

From a theoretical standpoint it is difficult to predict the course of the bainite formation below the M_s temperature. Elemendorf (19) produced varying amounts of martensite by quenching below the M_s temperature and then after raising to a temperature above the M_s temperature, allowed the remaining austenite to transform isothermally to bainite. It was found that the greater the amount of martensite the shorter the period of time before the beginning of the bainite formation. If the lag time for bainite formation below the M_s temperature is to be shorter than the one above, the martensite must not only accelerate the formation relative to the lag time above the M_s temperature but must also compensate for the normally longer lag times due to the lower temperature. If Greninger's (10) data is correct in having a greater rate of martensite formation when using lower quenching temperatures, then a high and low quenching temperature would give two initial amounts of martensite from which the transformation to bainite could be studied. It would seem that additional experimental work is needed to show the actual effect.

3. The Effect of Varying Amounts of Bainite on the M_s Temperature and on the Rate of Formation of Martensite.

Whereas the effect of martensite on the formation of bainite has been investigated, no data have been reported on the effect of various amounts of bainite on the martensite formation characteristics of the remaining austenite. In view of the increased importance of several heat treating processes closely connected with the M_s temperature and transformation of austenite into bainite just above this temperature, an investigation of this relationship would be important. In austempering, (30)(31), the complete isothermal transformation of austenite to bainite may not be carried out in which case the nature of the transformation of the remaining austenite would be important in relation to the final properties of the steel. In martempering (31) operations the steel is rapidly cooled to a temperature just above the M_s point and then held until the temperature is equalized between the interior and exterior after which the cooling is continued allowing the formation of martensite with less tendency for cracking. If the steel is held in the hot quench too long some bainite might form which would then change the austenite-martensite transformation.

Theoretically the effect of the bainite on the martensite formation would depend upon the effect of the bainite on the strain energy Δ E. If the bainite does not effect the strain energy, Δ E, or alter the austenite through changes of carbon content through diffusion, then the M_s temperature for the untransformed austenite should be the same. The rate of transformation of this austenite and the M_f temperature would be difficult to estimate. If, on the other hand, the amount of bainite is equivalent to the same amount of martensite, then the continuation of the transformation should be repressed to that temperature corresponding to the formation of an amount of martensite equal to the bainite originally present. The untransformed austenite would then start to form martensite and continue until the reaction was completed at the M_f temperature.

4. The Effect of Holding Times Just Above the M_s Temperature on the M_s temperature and the Rate of Formation of Martensite.

In the previous section thepossible effects of various amounts of bainite on the properties of martempered steels was considered. It would also be important to consider the effect of holding the austenite just above the M_s temperature for times up to those allowing bainite formation. No experimental work has been reported on this relationship for the plain carbon steels and only a few data on the alloy steels. Klier and Troiano (32) have investigated the M_s temperature in a number of chromium steels of various carbon contents. For a steel containing 15% Cr and 0.40% carbon, an interruption of several seconds at 395°C was sufficient to lower the M_s temperature from 72°C to slightly below room temperature. For a 15% Cr and 0.70% carbon steel they found a M_s temperature of -25°C when the samples were small slivers. If the size of the samples was increased to 1/4" cubes the M_s temperature was lowered to between -38° and -77°C due to the decreased cooling rates in the larger samples. Holding these samples at room temperature for one hour lowered the M_s temperature to below -77°C and holding for one year stabilized the austenite such that no further transformation occured on cooling down to liquid air temperatures.

Zmeskal (27) has shown that the M_s temperature of a high-carbon high-chromium steel may be lowered to below room temperature if quenched from 2200°F. Under these conditions he reports no stabilization on holding at room temperature while still in the completely austenitic condition. Theoretically it would seem that holding the austenite at these temperatures should have no effect on its transformation unless changes are occuring in the austenite which are not detectible.

5. Effect of Holding Times in the M_s-M_f Temperature Range on the Continuation of the Austenite-Martensite Transformation.

The noticeable effects of holding martensite-austenite mixtures at the temperature producing the mixture before continuing the transformation have become very important. This is particularly true when the M_f temperature is below room temperature thus allowing existance of the austenite-martensite mixture at room temperature. The retained austenite in these steels may transform after very long periods of time at room temperature or on additional cooling to subatmospheric temperatures. The degree of the completion of the transformation by further cooling is often restricted as will be shown. In either case the transformation will be accompanied by a volume change in the steel which in turn will produce certain dimensional changes in a finished part. The changes accompanying these transformations may be of a prohibitive magnitude in precision dies and gages.

In the early days of the tool steel industry, the steels were "stabilized" by a number of tempering operations, by storing for long periods of time or by alternate cycles of heating above room temperature and then cooling to subatmospheric temperatures. In this manner the austenite was completely transformed although the mechanism of the dimensional stabilization was not known. Gordon and Cohen (18) and Fletcher and Cohen (21) have summarized the work that has been done on the transformation of retained austenite both in regard to the nature of the transformation as such and on the resulting stability.

Gordon and Cohen have reported the results of an extensive investigation on the transformation of retained austenite in 18-4-1 high speed steel at substmospheric temperatures. They showed that holding the austenite-martensite mixture at room temperature for as short as two minutes caused a temperature lag before the transformation resumed and the greater the period of time at room temperature the greater the temperature lag. Even on continuous cooling the transformation stopped at -150°F leaving a small amount of permenently untransformed austenite. Holding times up to one hour did not reduce the final amount of transformation at -150°F although there was progressively less as the room temperature holding time was extended further. Their explanation of the phenomena was that "it is conceivable that even a relatively slight relief at room temperature of the austenite-martensite transformation stresses might have a profound effect on the resumption of the transformation during further cooling."

Fletcher and Cohen studied the same phenomena in a group of six steels including three of plain carbon analysis. The results were essentially the same as with the high speed steel in that longer times at room temperature produced greater temperature lags before the transformation continued.

They concluded that "conceivable, the stresses set up by the volume change accompanying the transformation facilitate the progress of the reaction on continuous cooling, and if the cooling is stopped within a suitable temperature range, enough stress relief might occur to alter the natural course of the decomposition when the cooling is resumed."

No data have been reported on the effect of holding at higher temperatures in the M_s-M_f range although the same results would be expected except at higher temperatures where the tempering of the martensite during the holding time might alter the subsequent transformation on cooling.

A working theory explaining these observations has not been developed. It is probable that the stabilization is associated with some change in the energy state of the nature of Zeners strain energy, Δ E.

6. The Effect of Time at the Austenitizing Temperature on the M_s Temperature and on the Rate of Martensite Formation.

Assuming no gross segregation, time at the austenitizing temperature should affect the transformation of the austenite to a degree depending upon the homogenity produced by the various heating times. The rate at which the austenite becomes homogenous at a given temperature will in turn depend upon the structure prior to heating. Thus a previously quenched sample will produce homogenous austenite more quickly than one originally composed of coarse pearlite.

This effect has been demonstrated by the work of Welchner, Rowland and Ubben (33) in which they found that the prior structure of a number of steels had a marked effect on the Jominy end-quench curve and that the differences due to the various initial structures persisted for rather long austenitizing times. Roberts and Mehl (34) studied the rate of formation of austenite and found that about 200 seconds at 850°C was sufficient to give homogeneous austenite in an eutectoid steel which had been normalized to give a fine pearlitic structure.

Even after the disappearance of the last visual particles of ferrite and carbide, there will be localized areas of high and low carbon. Since the M_s point is a function of the carbon content (10)(being lower for higher carbon contents), the transformation will start in the low carbon areas first and then progress to the high carbon areas as the temperature is lowered. Thus the non-homogeneous austenite would tend to produce the effect of raising the M_s point. After complete homogenization of the austenite there should be no further effect on either the M_s temperature or the rate of formation of martensite as the austenitizing time is increased.

7. The Effect of Varying Amounts of Martensite on the Transformation of Austenite Retained After Tempering.

If varying amounts of martensite are formed by quenching to temperatures in the M_s - M_f range and the samples then transferred to the tempering temperature, the effects of varying lengths of time to this temperature may be studied in relation to the transformation of this austenite to martensite on cooling. Elmendorf (29) and Fletcher and Cohen (35) have presented data showing the lengths of time that the austenite can be held at the tempering temperature before isothermal transformation to bainite begins for various amounts of martensite initially present. Times up to these limits could be used before again cooling in order to study the transformation of the remaining austenite. Theoretically it would seem that two possible effects could be realized. If the tempered martensite functions as bainite, then the conditions would be the same as discussed in section 3, i.e, considering the tempered martensite as supersaturated ferrite. If the time at the tempering temperature is insufficient for the body centered tetragonal structure to break down, then it would seem that the remaining austenite should start to transform after cooling to the initial temperature at which the martensite-austenite mixture had been formed the tempering thus having no effect. Should the time interval for tempering and again cooling to the initial temperature function to act as a holding time at temperature, then the result would be a stabilization of the austenite and there would be a temperature lag on further cooling before transformation would again start. The exact effect still needs experimental investigation.

Some of the more important variables which might effect the austenite-bainite and austenite-martensite transformations have been discussed. Where previous work of a similar nature had been done, a summary of this work was given. The theoretical aspects of the effects of the variables have been considered and possible theories proposed where possible. It is evident that the relationships have been inadequately considered particularly with reference to the plain carbon steels. The present investigation was confined to a study of some of the above variables on the transformation of austenite to martensite to bainite in an 0.83% and an 1.25% carbon plain carbon steel.

EXPERIMENTAL METHODS AND APPARATUS

Throughout this investigation, the quench-temper method of Greninger and Troiano (8) was used to produce structures in which the amounts of martensite formed as a result of a given set of conditions could be determined by microscopic examination. A few preliminary determinations showed that the following experimental conditions were essential to the reproducibility of results.

1. The samples must be completely uniform so far as chemical analysis is concerned, i.e., absolutely no segregation.

2. A non-carburizing, non-decarburizing and non-scaling atmosphere must be available for heating the samples to form homogeneous austenite.

3. Accurate temperature control of both the austenitizing furnace and the isothermal quenching baths.

The first two of these requisites are interrelated in that long soaking times at high temperatures are required to remove all segregation. During this long period of equalization of composition through diffusion, loss or gain of carbon must be prevented. To obtain these ends an inert nitrogen atmosphere furnace was developed which gave very satisfactory results.

The complete heat treating train including the isothermal quenching baths is shown in Fig. 2. Tube furnaces

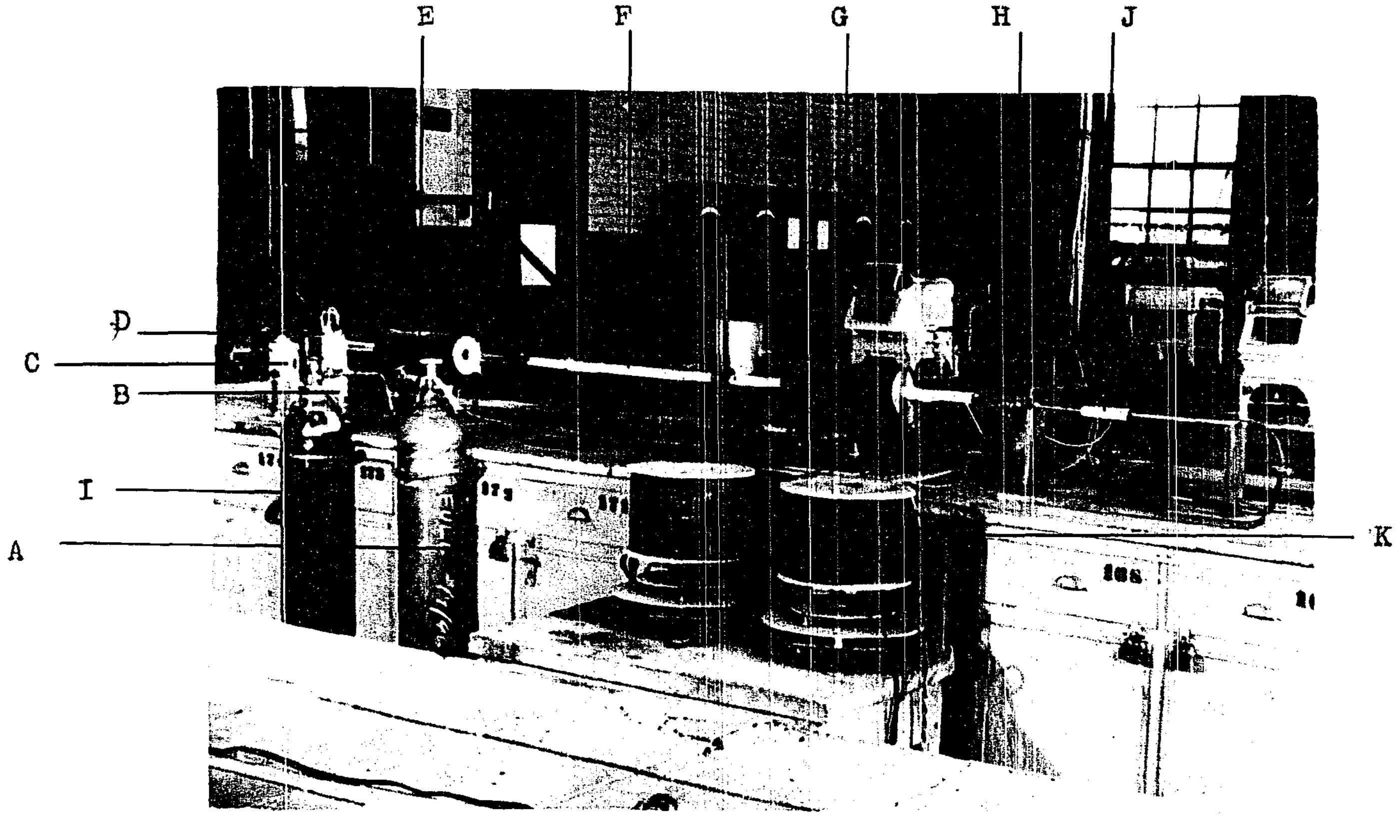


Fig. 2. Nitrogen Purification System and Furnace

A. Nitrogen Tank
B. Soda Lime
C. Sulfuric Acid
D. Glass Wool
E. Copper
F. Drying Agent
G. Austenitizing Furnace
H. Exhaust Bubbles
I. Hydrogen Tank
J. Charging Mechanism
K. Quenching Baths

were conveniently used because the samples to be treated were small and the temperature was more easily controlled.

For small scale experimentation, atmospheres of purified hydrogen, nitrogen and rare gases have been used. Hydrogen atmospheres produce excellent scale free surfaces on steels heated in it but at the same time it (36) has been shown to be highly decarburizing particularly in the presence of small amounts of moisture. Furthermore if it is necessary to frequently open the furnace to insert and withdraw samples, there is continual danger of sufficient back diffusion of the air to cause an explosion which fills the furnace with moisture. Purified rare gases serve excellently as inert atmospheres but their high cost is frequently prohibitive. The use of a vacuum furnace was impossible in this investigation because of the necessity of opening the furnace frequently and quickly to withdraw samples. With these limitations on the use of any of the atmospheres except nitrogen, the latter was used throughout the investigation.

Tank nitrogen processed to a purity of 99.97% for use in food handling was obtained in conventional 200 cubic foot cylinders. The main impurities were water vapor and oxygen with a possible trace of CO_2 and organic vapors. There was no positive evidence that the latter were present in any of the tanks used. This nitrogen from the cylinder (A in Fig. 2) was purified by first passing it through a tower of soda lime (B) to remove some water and any CO_2 that might be present. It was then more completely dried by bubbling the gas in series through two towers (C) containing concentrated sulfuric acid. In order to remove any entrained bubbles of acid, the nitrogen was passed through a tower (D) tightly packed with glass wool. There was no evidence that any SO_2 or SO_3 was picked up by the nitrogen as it was bubbled through the sulfuric acid.

The oxygen was removed from the gas stream by passing it through tightly packed copper turnings (E) held at 300°C. While no systematic experiments were run to determine the optimum temperature of operation for the copper, it was definitely shown that at 900°C the decomposition pressure of the copper oxide was sufficiently high to prevent satisfactory removal of the oxygen. The last traces of moisture were then removed by passing the gas through a one inch glass tube thirty inches long filled with anhydrous magnesium perchlorate.(F) From here it passed into the tube furnace (G) in which the samples were heated. In the heat treating furnace a plug of steel wool was placed just before the sample so that any impurities still in the nitrogen would react with it before reaching the samples. A thermocouple was imbedded in this steel wool so that the temperature could be checked on the interior of the furnace. From the heat treating furnace the nitrogen was exhausted to the air by bubbling through approximately two inches of concentrated sulfuric acid. (H) Fused silica tubes gave the most satisfactory results in the heat treating furnace.

The normal flow rate was about .015 cubic feet per hour. At this rate the copper turnings on the inlet side of the furnace would turn dark in about fifteen minutes. Apparently the oxide layer did not prevent the pick up of additional amounts of oxygen for after two days of operation the copper was discolored to a depth of only two inches. This indicated however that the copper would require periodic regeneration. To accomplish this, a tank of hydrogen(I) was connected into the gas line through a three-way stopcock so that either hydrogen or nitrogen could be fed through the system. Complete regeneration usually required about two hours. When determinations were being made each day, the copper was regenerated each night by passing the hydrogen through it. Flushing with nitrogen for one and one-half hours was sufficient to remove all of the hydrogen and place the train in usable condition.

In order to prevent oxidation of hot specimens being drawn from the furnace it was necessary to devise a method of moving the samples from the cold end of the tube into the hot zone and then out again without opening up the furnace. This was accomplished by attaching a small refractory boat (J) to the end of a thin strip of stainless steel. On the end of the stainless steel a three inch section of carbon steel was fastened and the two inserted into a small glas tube extending from a rubber stopper in the end of the silica tube of the furnace. A movable solenoid was placed around the glass tube such that it could be moved a sufficient distance to pull the boat in and out of the furnace when the proper current was passed through the coil.

The inertness of the atmosphere was checked by weight change determinations on steel samples heated in it. Small samples of the steel being studied were polished roughly to remove all scale and then cleaned in alcohol and dried. Handling the sample with tweezers, it was then weighed to the nearest 0.00001 gram on an assay balance. After weighing it was placed in the refractory boat in the cold end of the furnace. After flushing for at least ten minutes to remove air resulting from the opening of the tube, the sample was pushed into the hot zone of the furnace where it was allowed to remain for predetermined lengths of time at various temperatures. After the proper heating time the sample was removed from the furnace in two or three increments in order to prevent over heating of the end of the tube. Even under these conditions it was found advisable to increase the rate of gas flow in order to prevent any gases that might distill from the rubber to come in contact with the specimen. After the sample was completely cool it was removed from the boat and reweighed. With the train properly regenerated weight loss was less than 1 part in 30,000. For example, the weight loss on an 0.36519 gram sample of 0.80% carbon steel was 0.00001 grams after twelve hours at 2000°F. At lower temperatures and for shorter periods of time there was no measurable weight loss. For example two and one-half hours at 1900°F resulted in no weight change. The weighings were made very carefully, the weights not being removed from the balance pan between the weighings.

Under the above conditions the samples withdrawn from the furnace were perfectly bright and slightly etched due to the heat. It is interesting to note that slightly oxidized samples introduced into the furnace would come out bright due to the reaction of the oxide with the carbon of these steel. Under these conditions the samples would become decarburized although the atmosphere was inert. This fact illustrates the need for using scale free specimens in an inert atmosphere of this type.

During the course of the investigation, evidencesof decarburization were seen in the microstructure from time to time. When this condition was observed, the atmosphere was checked by running a weight change test. Invariably the sample would show an appreciable weight loss indicating decarburization due to the atmosphere. Examination of the train would show that a drying agent was exhausted, the copper was coated with oxide, or that the silica heat treating tube had become porous allowing air to diffuse into the furnace. The correlation of the weight change with the change in microstructure was thus established.

(K)

The isothermal transformation baths and the tempering baths consisted of 5 pounds of quaternary eutectic alloy containing Bi 50%, Cd 10%, Pb 27% and Sn 13%. These were heated in electrical pot furnaces, the temperature always being controlled to ± 1°C and usually to ± 1/2°C. Before transferring a sample to a bath, the oxide film was carefully scraped off so as to allow the maximum rate of cooling or heating of the specimen.

The experimental work of this investigation was confined to a study of two plain carbon steels of the following analysis:

Nominal Analysis	% C	% Mn	% S	% P	% Si
0.80% C	0.81	0.62	0.023	0.012	0.19
1.25% C	1.26	0.28	0.007	0.017	0.30

Both of these steels were obtained in the form of polished drill rod 0.180" in diameter. These rods were cut up into thin discs about 0.040" thick, the size used in all of the determinations. About 75 of these samples were placed in the refractory boat of the furnace along with a weighed test sample. After flushing the furnace the boat full of samples was pushed into the hot zone and held for 12 hours at 2000°F. The samples were then removed and the test sample reweighed as a check on the atmosphere during the homogenizing period. As samples were needed they were homogenized in batches in this manner, a test sample being run with each batch.

Individual homogenized samples were then fastened to the end of an 0.065" nickel wire so that they could be heated to the proper austenitizing temperature and then transferred to the proper metal bath for study of the transformation. The burr left on the samples by the hack saw was notched by a jewelers saw. An 0.003" stainless steel wire was twisted around this notch and then threaded through a hole in the end of the nickel wire thus fastening the two together. Greninger (37) has estimated that samples of this size should reach the bath temperature in about two seconds.

The actual sequence of quenching for the various determinations will be discussed in the next section. The general procedure however was as follows: The sample fastened to the end of the nickel wire was inserted into the austenitizing furnace maintained at the proper temperature. As the sample was being inserted the flow rate of the nitrogen was increased and was not decreased until two or three minutes after the rubber stopper had been reinserted into the silica tube. It was found that if this precaution was not taken, enough air diffused back into the furnace to cause decarburization. The cold end of the nickel wire was inserted into the rubber stopper so that the sample would be suspended in the gas stream and would not touch the sides of the tube. After the proper length of time of heating in the austenite field, the sample was removed and rapidly plunged into the bath at the proper temperature for transformation. After the proper transformation time, the sample was quickly transferred to the tempering bath and then quenched into a dilute sodium hydroxide solution for final cooling. In this manner any untransformed austenite changed to martensite or, if the M_f temperature was below room temperature, remained as austenite. On etching out, only the areas transformed at the time of tempering will turn black, the white areas, therefore, representing untransformed austenite. All the austenitizing times were 30 minutes unless otherwise noted and the tempering times were five to six seconds. The low temperature studies were made by quenching into an ice-ammonium chloride mixture contained in a Dewar flask. Temperatures of -15°C were easily produced. In all instances less than one second was required to transfer the samples from one bath to another.

The samples were then mounted individually by pressing them into an 0.180" hole drilled into a 1/2" cube of low carbon steel. Careful polishing was essential to prevent any tempering of the martensite that might be present in the specimen. The samples were rough polished until about half of the specimen was removed so that final examination would be in the center of the specimen. Polishing was completed by taking the specimen through the finer grades of paper, onto a wax wheel with 600 alundum and finishing up with levigated alumina. A slight etch and repolish seemed to produce better final structures.

The photometric method developed by Saunders and Kahles (9) was used to determine the percentages of transformation in the sample. The success of the method depends almost entirely upon the etching since as high a contrast as possible is required between the tempered and untempered transformation products. The following new etching agent was developed:

Absolute Alcohol	200 ml.
Urea	11 g.
Fuming HNO_3	44 ml.

By using absolute alcohol and fuming nitric a minimum of water was present in the final etching solution. The urea reduces the staining tendencies of the etching solution probably through reaction with the oxides of nitrogen which are formed as a result of the etching reaction and which may be present in the original acid.

The polished samples were etched in this solution for lengths of time depending upon the thermal treatment that had been applied to the sample. In general the greater the amount of tempered reaction product the greater the length of time required for a satisfactory etch. The time generally varied between 22 seconds for samples with small amounts of tempered product to 50 seconds for samples representing complete transformation. The samples were quickly rinsed by dipping the sample successively into two containers of absolute alcohol and then dried in an air blast, the air having passed through a drying agent to remove moisture. A given amount of etching solution was used for only two samples and then replaced. This was necessary since continued use of the etching solution caused staining.

The amount of transformation in each sample was determined photometrically using an electron tube photometer. The ocular for the camera attachment to the microscope was removed and the phototube placed at this point. With a 21X objective in the microscope, the image on the phototube corresponded to a circular area on the sample having a diameter of 0.018", i.e., about one-tenth the diameter of the sample.

The instrument was standardized and the determinations made as follows: A carefully polished, as quenched, unetched sample was used as the standard for setting the instrument. This sample was placed on the stage of the microscope and focused as for visual examination. The image of this surface was then shifted to the phototube which in turn activated the galvanometer which had a scale calibrated into 100 arbitrary units. By means of the aperture diaphram on the microscope and the sensitivity control on the photometer, the instrument was set to read 100. This setting was always checked before and after taking readings. So long as there were no gross changes in the line voltage the tungsten target bulb in the microscope served as a very constant light source. The as quenched sample was then etched for about 20 seconds in order to produce over the entire sample an amount of etching which would correspond to the etching of the untransformed portion of the samples on which a percentage transformation was being made. This sample gave a reading of 96 on the photometer and was used thereafter to represent the value for a sample showing 0% transformation. Another sample was then completely quenched and then tempered. After etching, a reading of 9 was obtained and this value was used to represent a sample 100% transformed. Partially transformed samples gave photometer readings between these two limits and the percent transformations could be calculated accordingly.

It is obvious that if the photometric method is to give correct results, the transformed portions of the samples must etch to the equivalent of the completely transformed sample and the untransformed portion to that of the completely untransformed sample. This requires etching to a maximum contrast in the samples. If the samples are underetched, the transformed portions will be too light and consequently the photometer reading too high. If the sample is overetched, the untransformed sections will be too dark and the photometer reading will be correspondingly low. Saunders and Kahles have shown that if the readings obtained on the same sample after different etching times is plotted against the time of etching, a characteristic etching curve is obtained. As etching progresses the reading drops due to the darkening of the transformed sections of the samples. Finally a point is reached at which the sample can be etched for an increasing period of time without the reading changing, i.e., the contrast remains constant. Longer etching times caused the untransformed background in the samples to stain and the reading to drop.

After etching a number of samples, enough experience was gained so that an etch giving maximum contrast could be recognized visually without running a complete etching curve. It might be stated that a completely transformed sample cannot be etched to give an absolutely uniform darkening but rather some portions tend to be slightly brownish. This same conditions existed in the transformed areas of the partially transformed samples so that the readings obtained on any sample do give the correct calculated amount of transformation. It was essential in each case that the light portions of the structures show absolutely no staining for this affected the reading much more than the slightly brownish color of parts of the transformed portion.

DISCUSSION OF THE EFFECTS OF THE SEVERAL VARIABLES ON AUSTENITE-BAINITE AND AUSTENITE-MARTENSITE TRANSFORMATIONS

In this section the experimental results of this investigation will be discussed. Each variable will be considered in the same order as it was considered in the section on the importance of the various variables. In each case the experimental details peculiar to the study of the stated variable will be stated. The experimental results will then be presented and discussed.

1. The Effect of Austenitizing Temperature on the M_s Temperature and on the Rate of Martensite Formation Below the M_s Temperature.

The effect of the austenitizing temperature was investigated with relation to the 0.80% carbon steel only because of the presence of carbides when the 1.25% carbon steel was quenched from lower temperatures. Austenitizing temperatures of 1050°C, 815°C, 760°C and 735°C were used. A number of samples were quenched from these temperatures into the metal baths at a series of temperatures in order to locate the M_s temperature. Microscopic examination of these samples showed that it was difficult to exactly state the temperature at which the martensite had started to form although the first temperature at which there was a general distribution of needles could be determined to within about 2°C. On the basis of the first general distribution of needles, the following experimental values were obtained for the M_s temperatures:

Austenitizing Temperature	M_s Temperature
1050°C	242°C
815	242
760	228
735	225

As an example of the range of temperature over which some martensitic needles may be found, it was possible to find one or two martensitic needles in a sample austenitized at 760°C and quenched to 242°C although there was not a general beginning until the temperature had been lowered to 228°C. This condition is shown in Figure 3. The structures obtained for the various austenitizing temperatures and at the respective M_s temperatures are shown in Figures 4, 5, and 6. It is to be noted that there are distinct differences in the nature of the martensite formed from high temperature austenite as compared to that formed from austenite just above the critical temperature. It was generally noted that the high quenching temperatures caused long well defined needles of martensite to form while low quenching temperatures produced shorter less distinct needles.

The data show that the M_s temperature increases as the quenching temperature is raised up to about 800°C and

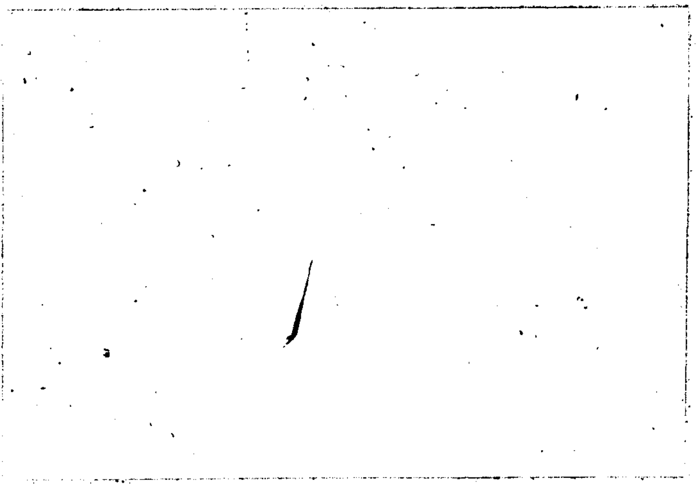


Fig. 3. Small needle of martensite formed on quenching 0.80% C Steel to 242°C. Aust. Temp. 760°C 300X

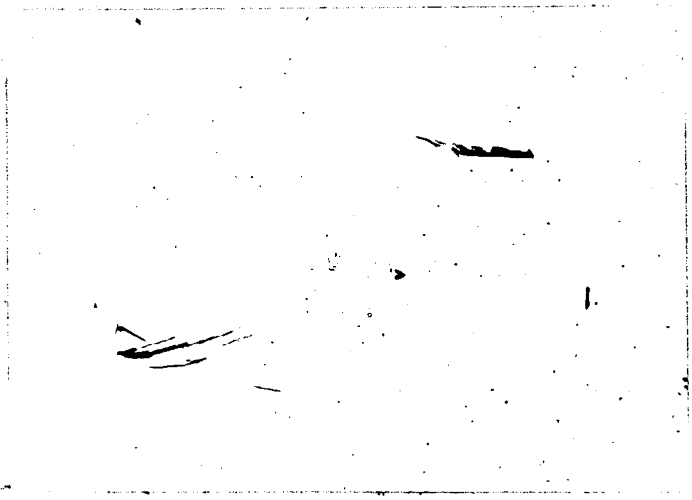


Fig. 4. Transformation at M_s temperature 242°C, for 0.80% carbon steel. Aust. Temp. 1050°C. 300X

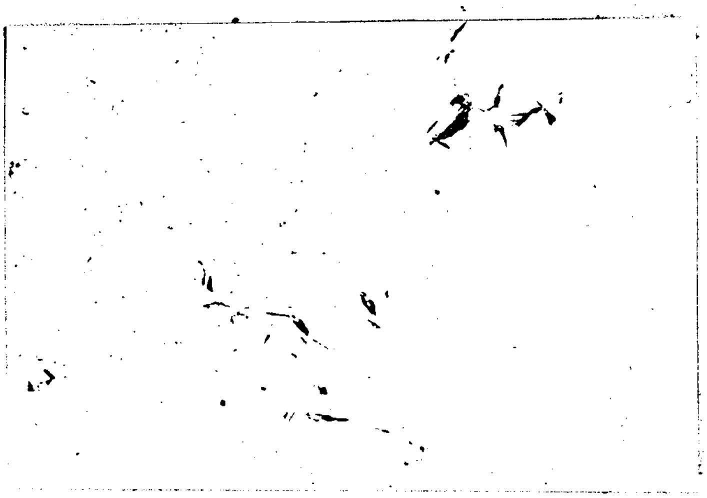


Fig. 5. Transformation at M_s temperature, 227°C, for 0.80% carbon steel. Aust. Temp. 760°C. 300X

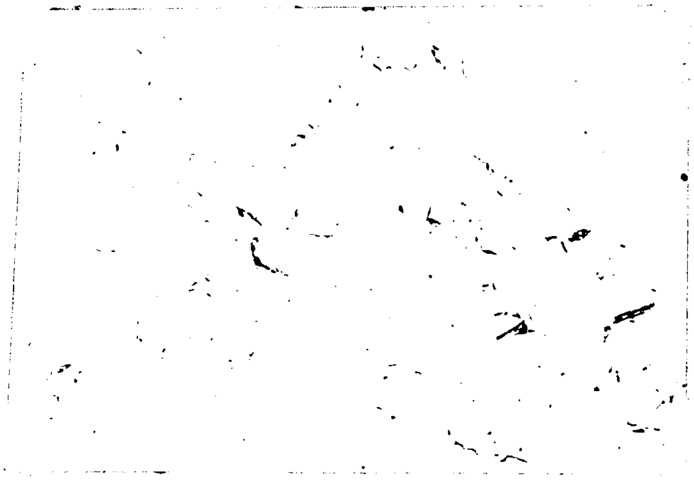


Fig. 6. Transformation at M_s temperature, 225°C, for 0.80% carbon steel. Aust. Temp. 735°C. 300X

thereafter is constant up to 1050°C. Figure 7 shows the effect of these quenching temperatures on the amounts of martensite formed at various temperatures below the M_s temperature. It is to be noted that at each quenching temperature, the amount of martensite formed is greater for the quenching temperatures below 815°C. The only exception applies for quenching temperatures just below the M_s temperature for the samples austenitized at 735°C and 760°C. The data are incomplete but at 226°C are probably very close to the values represented by the dotted curve. In this temperature range the higher M_s temperature of samples quenched from 1050°C allows enough martensite to form to more than compensate for the faster rate of martensite formation just below the M_s temperature for samples quenched from the lower temperatures.

In Figure 8 these data are plotted in the form of rate of martensite formation curves. The percent transformation of austenite to martensite is plotted as the ordinate against the number of degrees below the M_s temperature required to form the respective amounts of martensite as the abscissa. There are two interesting points brought out in these curves. In the first place, the lower the quenching temperature the greater the initial rate of formation and, secondly, beyond about 30% transformation, the rate of transformation is constant for all austenitizing temperatures. This latter point is shown by the equal slopes of the curves. It is interesting to note further that the higher quenching

Fig. 7
Effect of Austenitizing Temperature
on Martensite Formation
0.80% C Steel

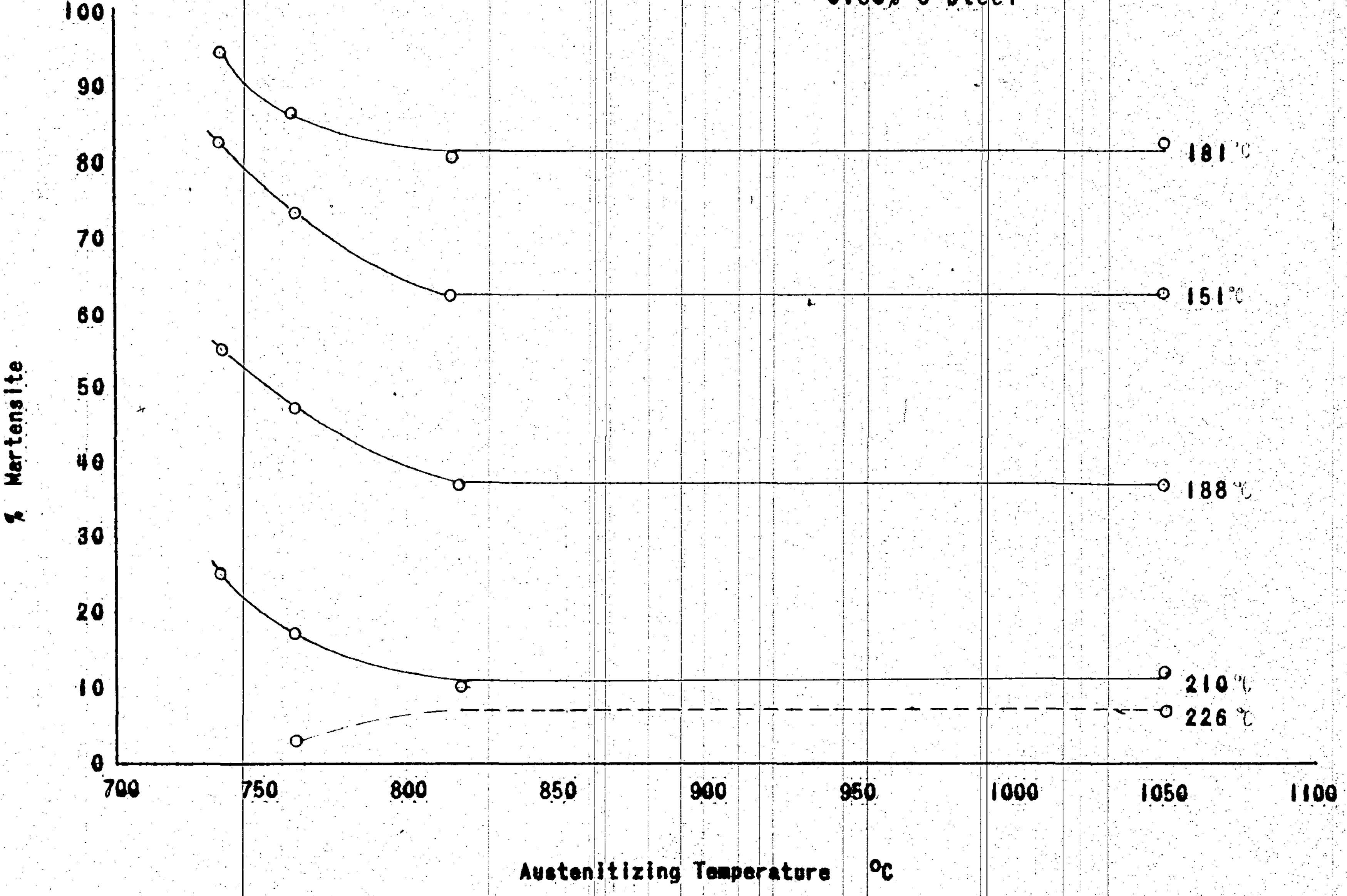
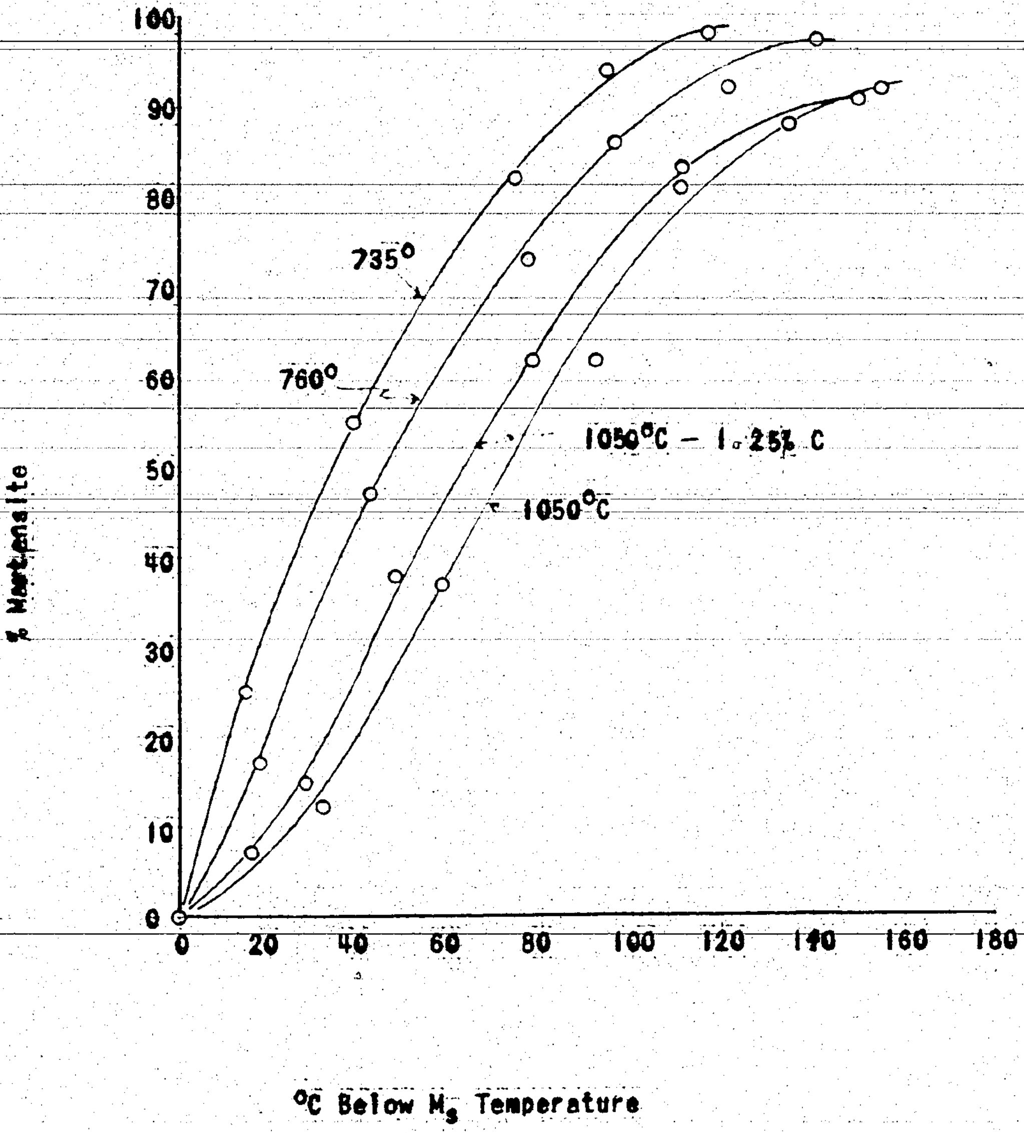


Fig. 8
Effect of Austenitizing Temperature
on Martensite Formation
0.80% C Steel



temperature gives both a higher M_s temperature and a lower M_f temperature, the transformation therefore extends over a greater temperature range.

It is felt that these results reflect a true temperature effect as well as a grain size effect. Since the martensite forms from austenite through a mechanism of shear with a whole section of the austenite crystal transforming at once, then the length of a martensite plate or needle would be restricted to the diameter of the austenite grain. That this is apparently true may be seen by examination of Figures 4, 5, and 6. In addition there must be a true temperature effect since the amounts of transformation at any temperature below the M_s point are the same for quenching temperatures above 815°C. On heating above 815°C grain growth occurs which does not seem to have any effect on the transformation. The grain size at 760°C was 6-7 and at 1050°C, 1-2. In general it was more difficult to etch the samples quenched from the lower temperatures and a careful examination of the surface showed that it contained a number of very small particles or pits which could not be resolved. Since they were present in some samples more than others it would seem that they were very small etch pits. That they were not undissolved carbide particles, may be shown by two arguments. Long times at the austenitizing temperature had no effect on the etching characteristics and the 0.80% carbon steel should be in the austenite field. If anything free carbides would be present and these in depleting the austenite of its carbon would raise the M_s temperature rather than lower it. For want of more definite experimental evidence, it may be stated that according to Zener's views on the martensite formation, the lower austenitizing temperatures in some manner increases the amount of strain energy, Δ E, required to initiate the martensite formation and thus lowers the M_s temperature.

Only one austenitizing temperature (1050°C) was used in studying the rate of martensite formation in the 1.25% carbon steel. The data are given in Table II and plotted in Figure 8. The transformation was not complete at -15°C, the lowest temperature studied.

2. Effect of Martensite on the Formation of Bainite Below the M_s Temperature.

The isothermal transformation of the austenite remaining after quenching to various temperatures below the M_s point was studied for the 0.80% carbon steel for austenitizing temperatures of 760°C and 1050°C. No studies were made on the 1.25% carbon steel because of the extremely long times involved even before the bainite formation starts. For example, at the M_s temperature the bainite transformation was only 25% complete at the end of 24 hours. At lower temperatures the times would be much longer.

It has been shown that by using austenitizing temperatures of 760° and 1050°C, different amounts of martensite will be formed for the same temperature below the lowest M_s temperature. If the untransformed austenite at this temperature is then allowed to transform, isothermally, then the progress of the reaction may be studied under the influence of two different amounts of martensite. It is possible that other variables may be involved which cannot be isolated from the effect of the martensite. In particular, the variables which caused the difference in the amount of martensite might have their effect on the bainite reaction as such. These variables were discussed in connection with the effect of austenitizing temperature on the martensite formation and included the possible effect of grain size and differences in the solid solution austenite which can not be detected experimentally.

These transformations were studied at 242°, 226°, 210°, 186°, 151° and 131°C (Table I). These results are presented graphically in Figures 9 to 14 for austenitizing times of 760°C and 1050°C as shown. In each case the horizontal portion of the curve indicating no change in transformation with time represents the amount of martensite that formed on cooling the austenite down to the isothermal temperature at which the progress of the bainite reaction was to be studied. In Figure 9 the curves for the transformation refer to an isothermal temperature of 242°C which is above the M_s temperature for the samples austenitized at 760°C. Consequently the transformation curve for this quenching temperature gives the progress of the transformation from all austenite to all bainite. The curve for samples quenched from 1050°C gives the transformation of the remaining bainite after about 1% or 2% of martensite had formed. The data show that a given amount of bainite forms in a shorter period of time when the higher quenching temperature is used. it is generally considered (7) that higher quenching temperatures move the beginning of the various isothermal transformations to longer time periods although the effect is less for the bainite reaction. In the steel studied the actual difference is rather small and that the higher temperatures gives smaller lag times may be due to the nucleating effect of the small amounts of martensite.

At 226°C the two curves still retain their same relative positions both austenitizing temperatures producing some martensite before the beginning of the bainite transformation. At and below 210°C however the greater rate of martensite formation due to quenching from 760°C causes the positions of the two curves to shift. At these temperatures a given <u>total</u> amount of transformation occurs in a shorter time when the lower austenitizing temperature is used. It is to be noted that the curves for each isothermal decomposition temperature are almost parallel and that they may be made to almost coincide if the bainite reaction is corrected for the differences in the initial amounts of martensite. This is brought out more clearly if the data for the bainite

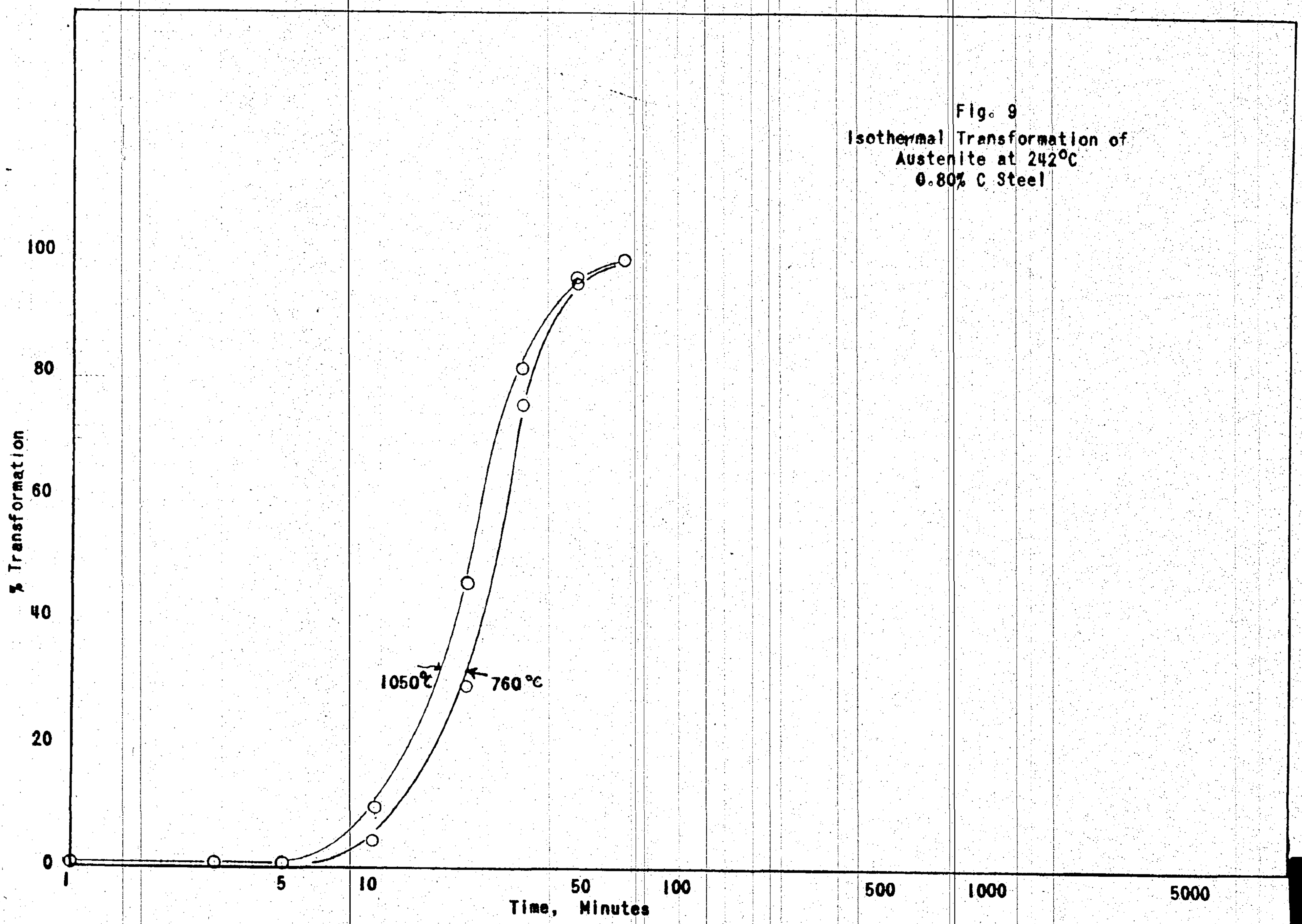


Fig. 9
Isothermal Transformation of
Austenite at 242°C
0.80% C Steel

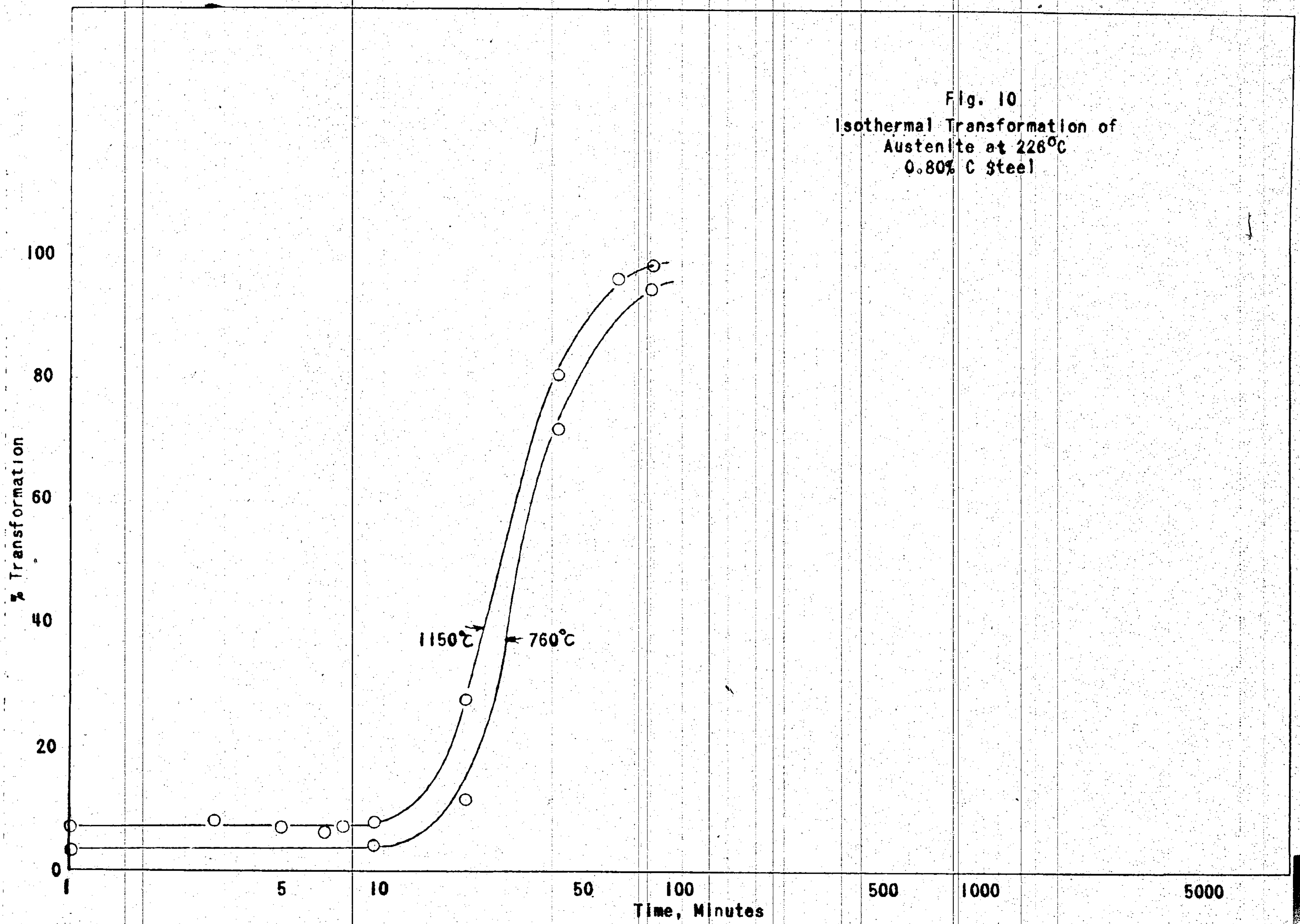


Fig. 10
Isothermal Transformation of
Austenite at 226°C
0.80% C Steel

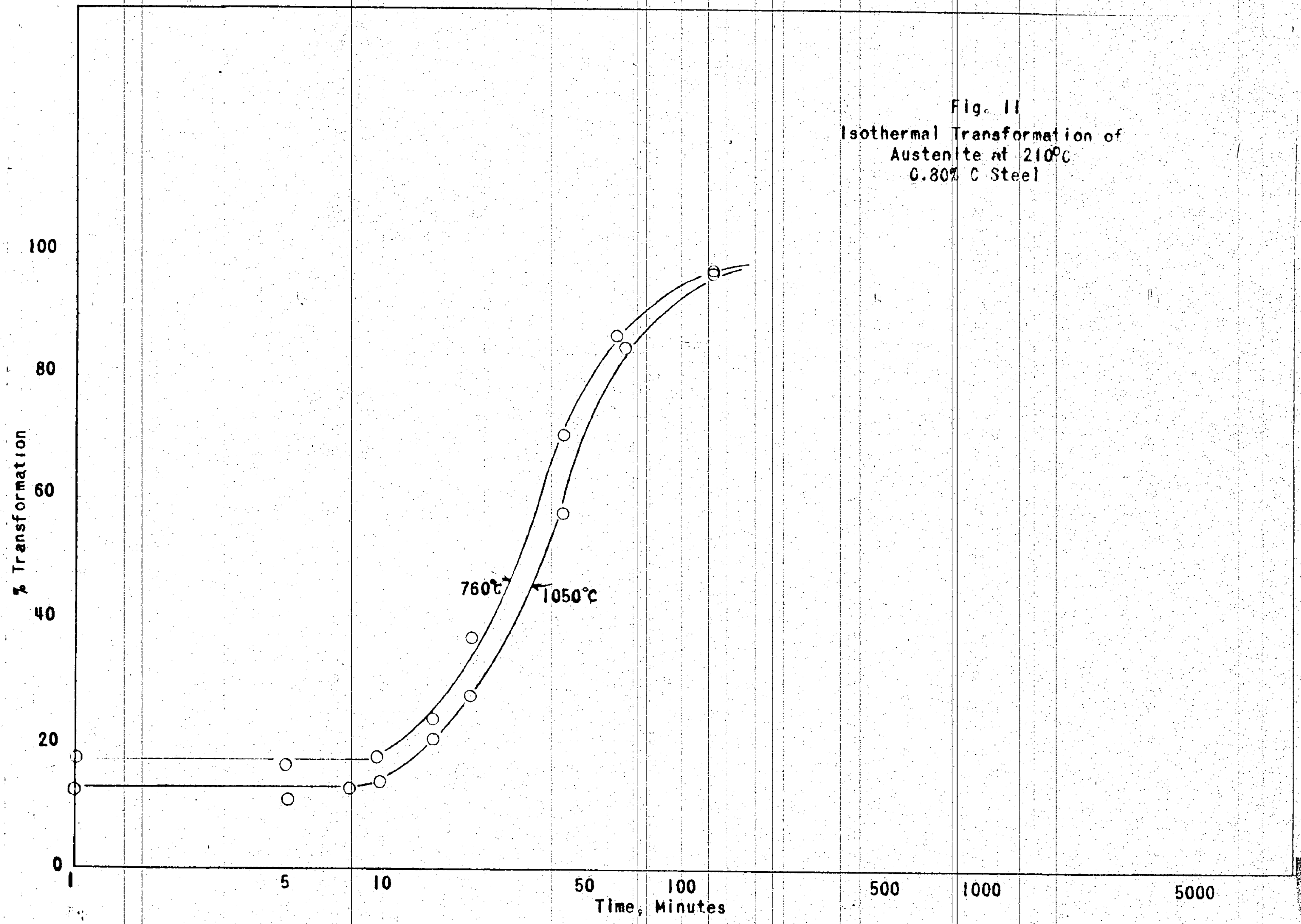


Fig. 11
Isothermal Transformation of
Austenite at 210°C
0.80% C Steel

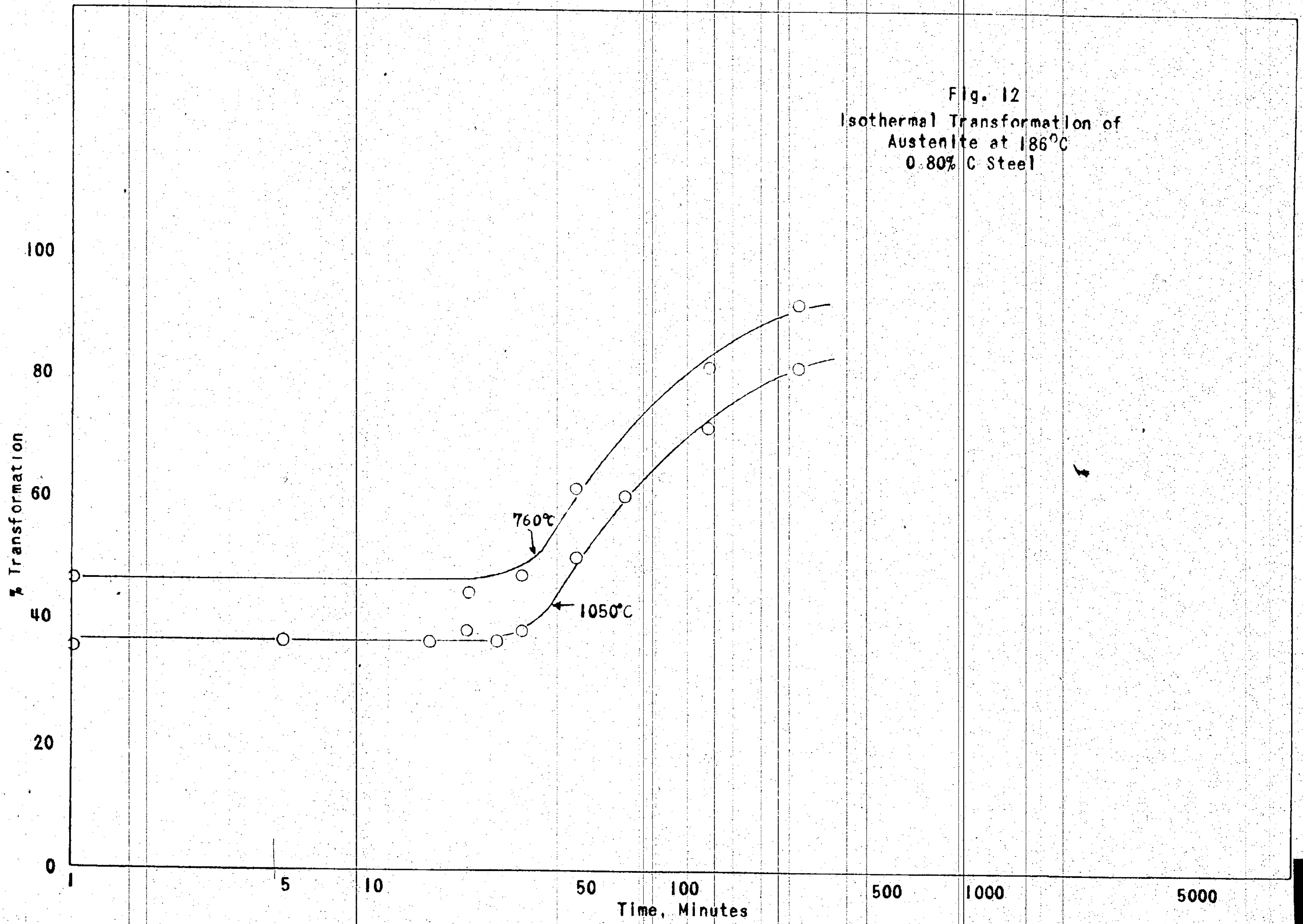


Fig. 12
Isothermal Transformation of
Austenite at 186°C
0.80% C Steel

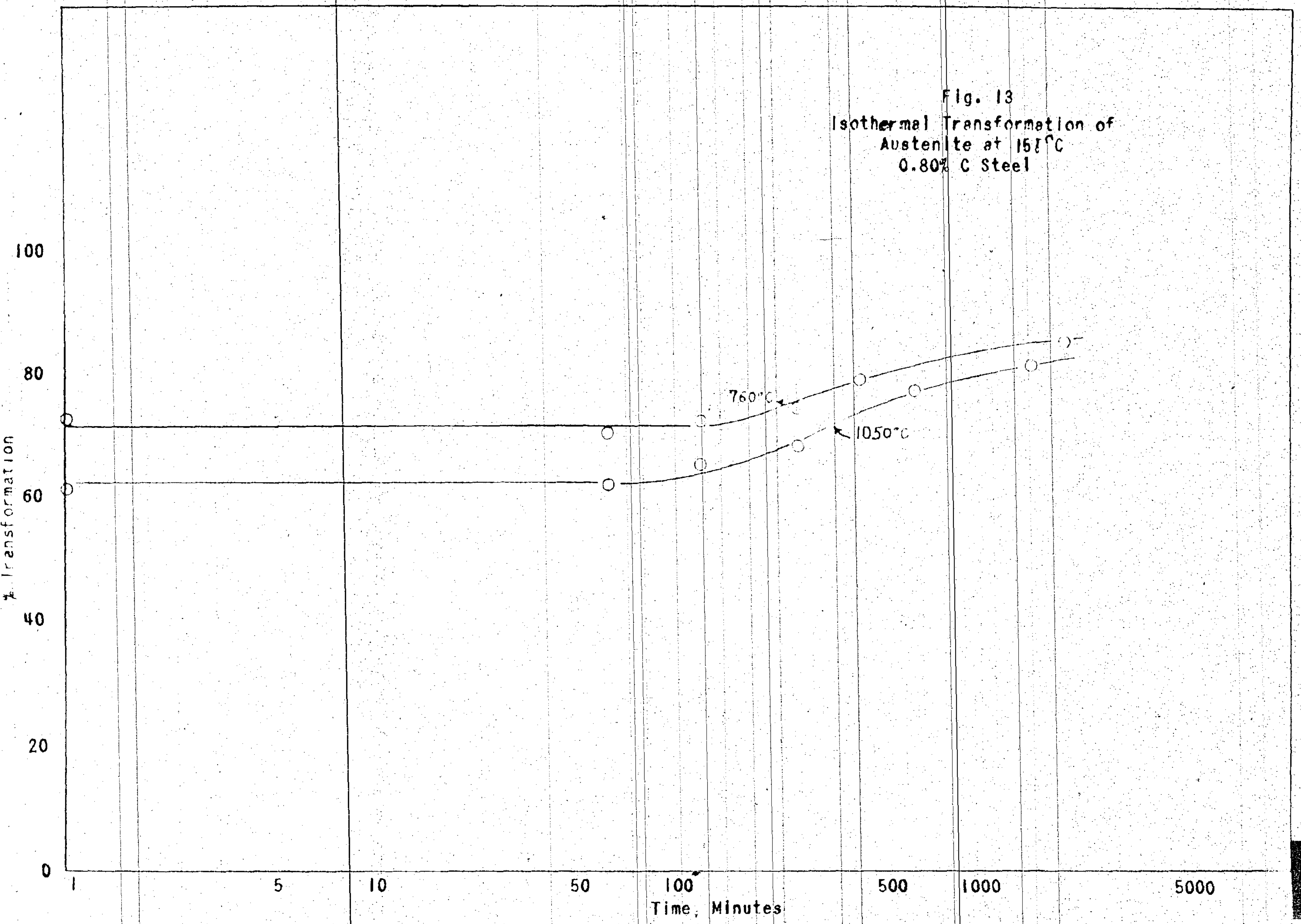


Fig. 13
Isothermal Transformation of
Austenite at 151°C
0.80% C Steel

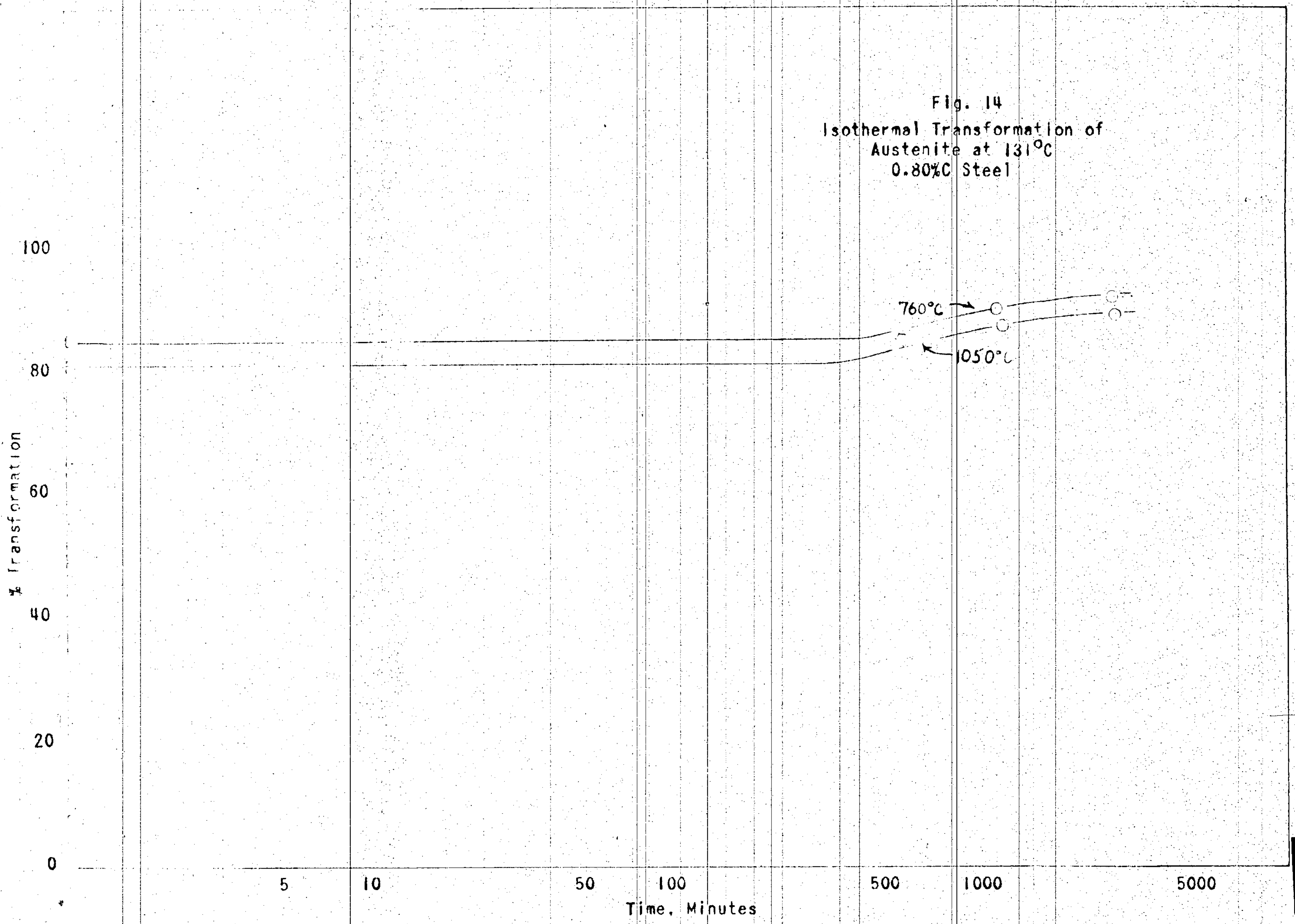


Fig. 14
Isothermal Transformation of
Austenite at 131°C
0.80%C Steel

transformation is taken alone and plotted as a continuation of the conventional time-temperature-transformation curve into the martensite region as shown in Figure 15. The beginning times and the times for 50% transformation of the remaining austenite after the formation of martensite are plotted. The extremely long times required for the completion of the reaction at the lower temperatures prevented the determination of the ending times. Some of the structures resulting from austenitizing at 1050° and 760°C and isothermally transforming at 186°C are shown in Figures 16 to 21.

With the exception of transformation at 210°C, the curves for the two different austenitizing temperatures almost coincide. Around 210°C the presence of martensite seems to accelerate the formation of bainite, causing the transformation to start at about the same time it had at slightly higher temperatures. Elmendorf (29) has shown that various amounts of martensite will increase the rate of transformation of austenite above the M_s temperature. Here it would seem that the rate of martensite formation just below the M_s temperature is too low to effect the bainite formation until 7% or 8% is formed at 226°C. As the temperature is then dropped to 210°C enough martensite forms to accelerate the formation of bainite and thus cause a sharp change in the slope of the curve representing the beginning of bainite formation at various temperatures. When an austenitizing temperature of 760°C is used the M_s point is lower but the

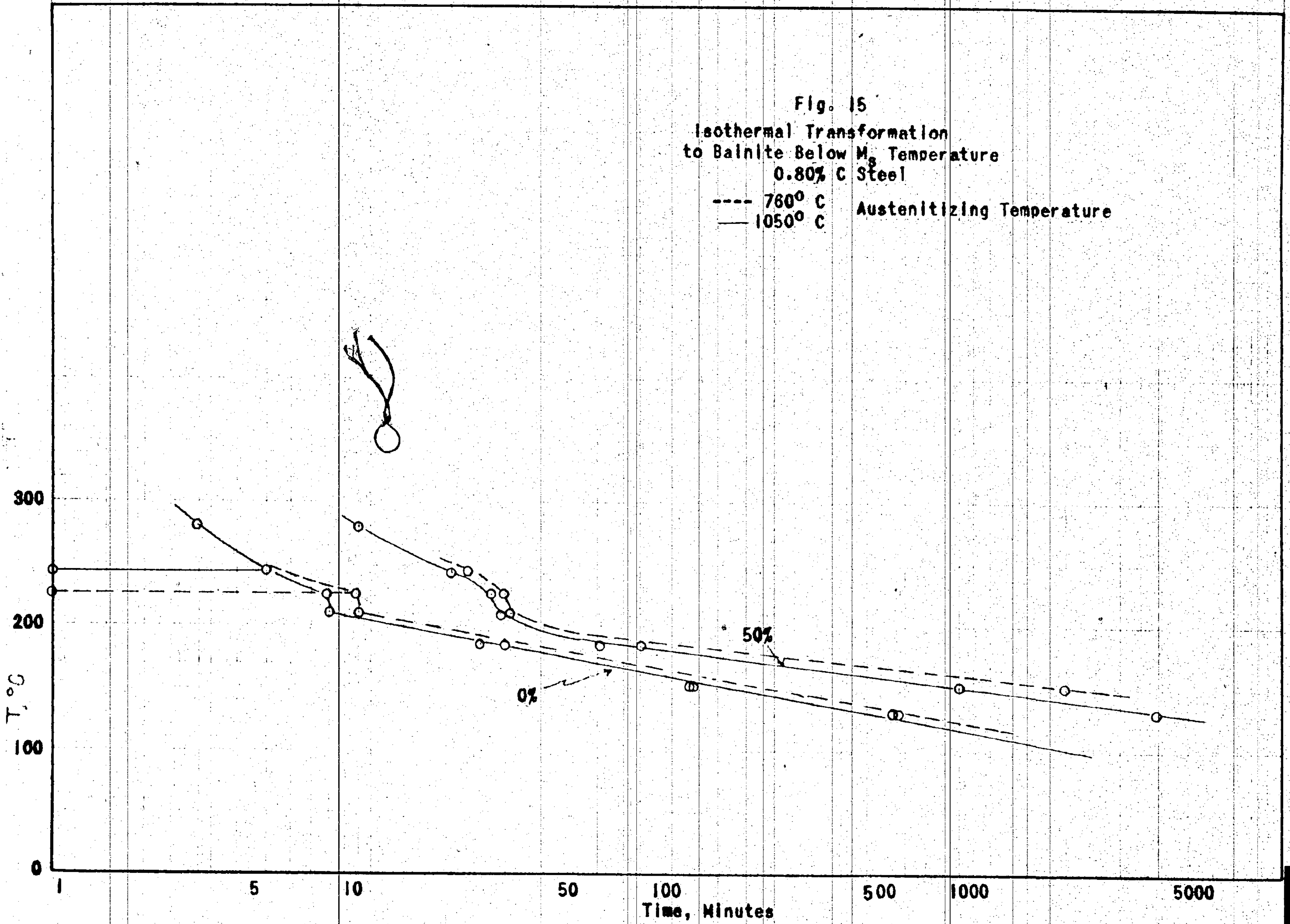


Fig. 15
Isothermal Transformation
to Bainite Below M_s Temperature
0.80% C Steel

Fig. 16. Martensite formed on cooling 0.80% carbon to 186°C. Aust. Temp. 1050°C. 36% martensite. 300X

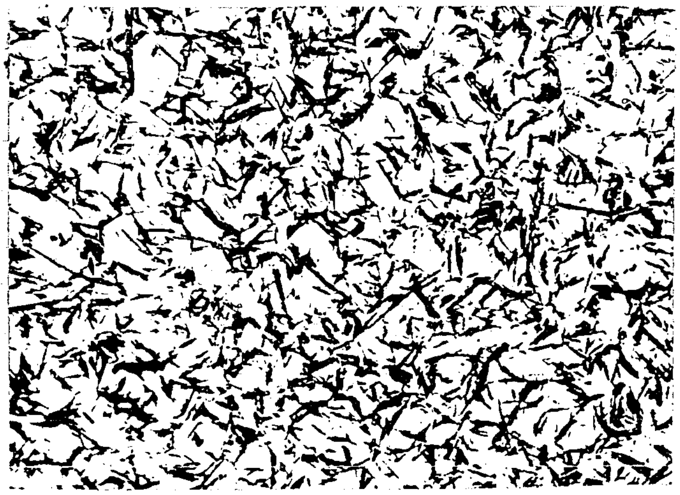


Fig. 17. Same as Fig. 16. Aust. Temp. 760°C. 47% martensite. 300X

Fig. 18. 0.80% carbon steel quenched to 186°C. Held 45 min. Aust. Temp. 1050°C. 51% Transformation. 500X

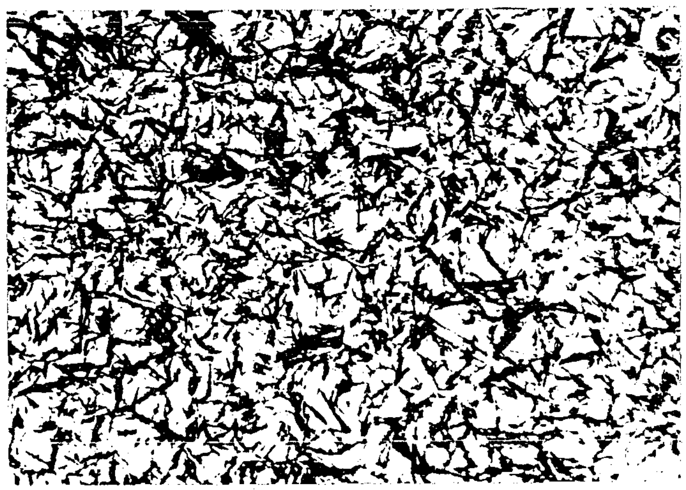


Fig. 19. Same as Fig. 18. Aust. Temp. 760°C. 62% Transformation. 500X

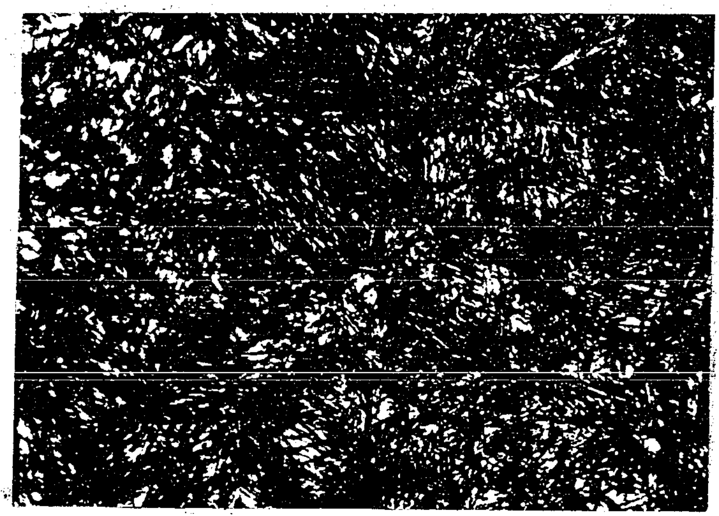


Fig. 20. Same as Fig. 18. Time 240 minutes. 82% Transformation. 300X

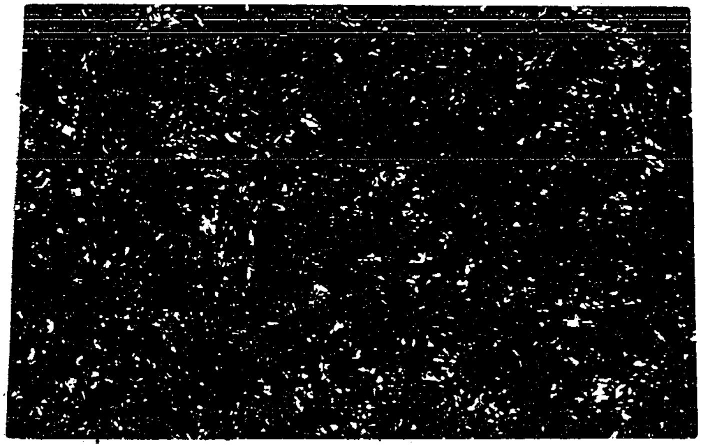


Fig. 21. Same as Fig. 19. Time 240 minutes. 92% Transformation. 300X

rate of martensite formation just below this temperature is higher resulting in an almost immediate effect on the bainite formation. This effect is still evident in the 50% transformation curves.

It is felt that the relative insensitiveness of the bainite reaction to austenitizing temperature (and hence grain size) reflects further the difference between the pearlitic types of transformation and the bainitic types. Pearlite is known to nucleate at the grain boundaries and to grow as a result of the diffusion of carbon. The bainite reaction seems to start more throughout the grains and if it is transformation of austenite into ferrite of the same carbon content then the amount of carbon diffusion required for the transformation should be small. The actual grain size should thus have little effect on the trans formation as is brought out in the data.

3. The Effect of Varying Amounts of Bainite on the M_s Temperature and on the Rate of Formation of Martensite

The effect of various amounts of bainite on the transformation of the austenite remaining after partial bainite formation was studied for both the 0.80% and 1.25% carbon steel. The temperature used for formation of bainite in the 0.80% carbon was just at the M_s temperature, 242°C. By using transformation times of 10, 20, 25, and 30 minutes samples containing 10%, 47%, 72%, and 82% bainite were obtained. The microstructures are shown in Figures 22, 23, and 24. These amounts of bainite were formed by quenching at 242°C and the martensite transformation characteristics of the remaining austenite were studied by quenching the bainite samples to various lower temperatures. If the amount of bainite present at the time of quenching is plotted against the amount of martensite formed on cooling to various temperatures, a series of straight lines result as shown in Figure 26.

There are two things to be noted in these curves. In the first place the lines for the amount of martensite formed at a given temperature from various austenite-bainite mixtures are parallel showing that the same effect is involved at all decomposition temperatures. In the second place, the bainite replaces the martensite almost one to one, in each case, lowering the temperature at which martensite starts to form. Thus with 50% bainite present, the remaining austenite will not start to transform until the sample is cooled to a temperature corresponding to the formation of 50% martensite. The intercepts of these lines with the abscissa gives the M_s temperature of the remaining austenite after the respective amounts of bainite have formed. Figure 25 shows the microstructure for the 82% bainite sample quenched to 131°C. It is evident that if the austenite had started to transform on cooling at the original M_s temperature, then transformation would have been completed much above 131°C.

Fig. 22. 0.80% carbon steel isothermally transformed for 10 minutes at 242°C. Aust. Temp. 1050°C. 10% Bainite. 300X

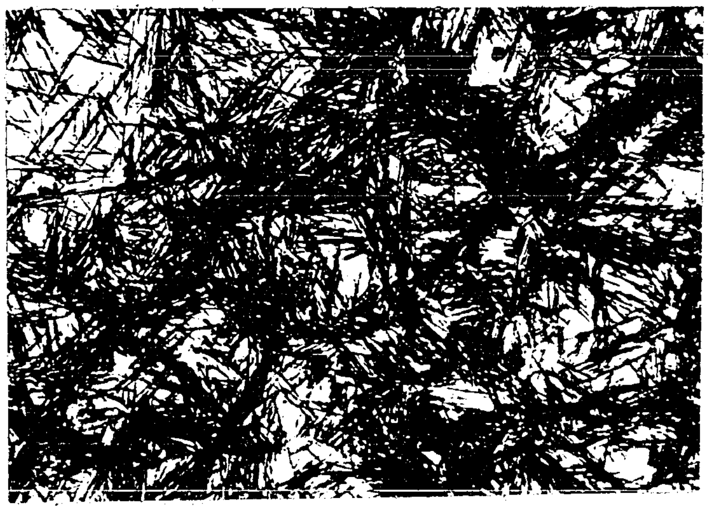


Fig. 23. Same as Fig. 22. 20 minutes. 47% Bainite. 300X

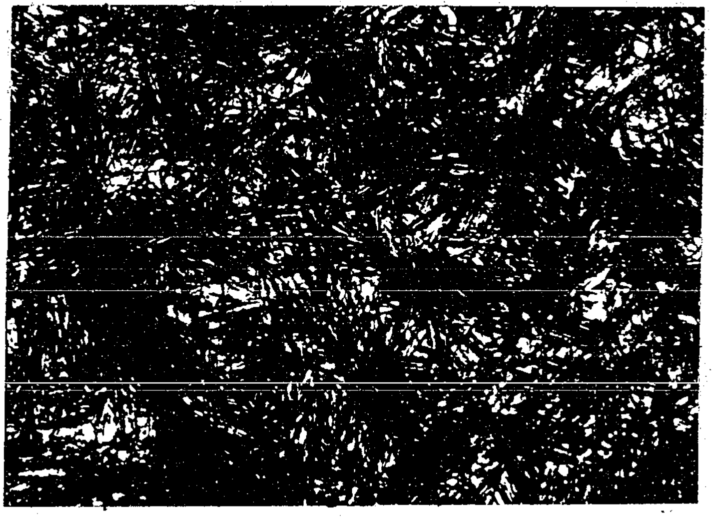


Fig. 24. Same as Fig. 22. 30 minutes. 82% Bainite. 300X

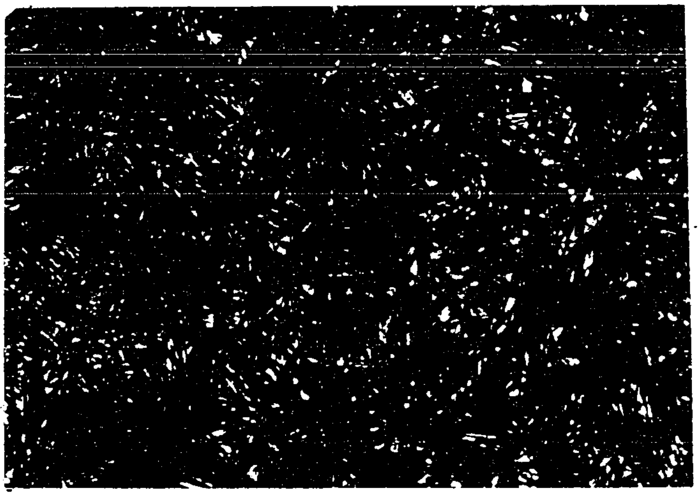
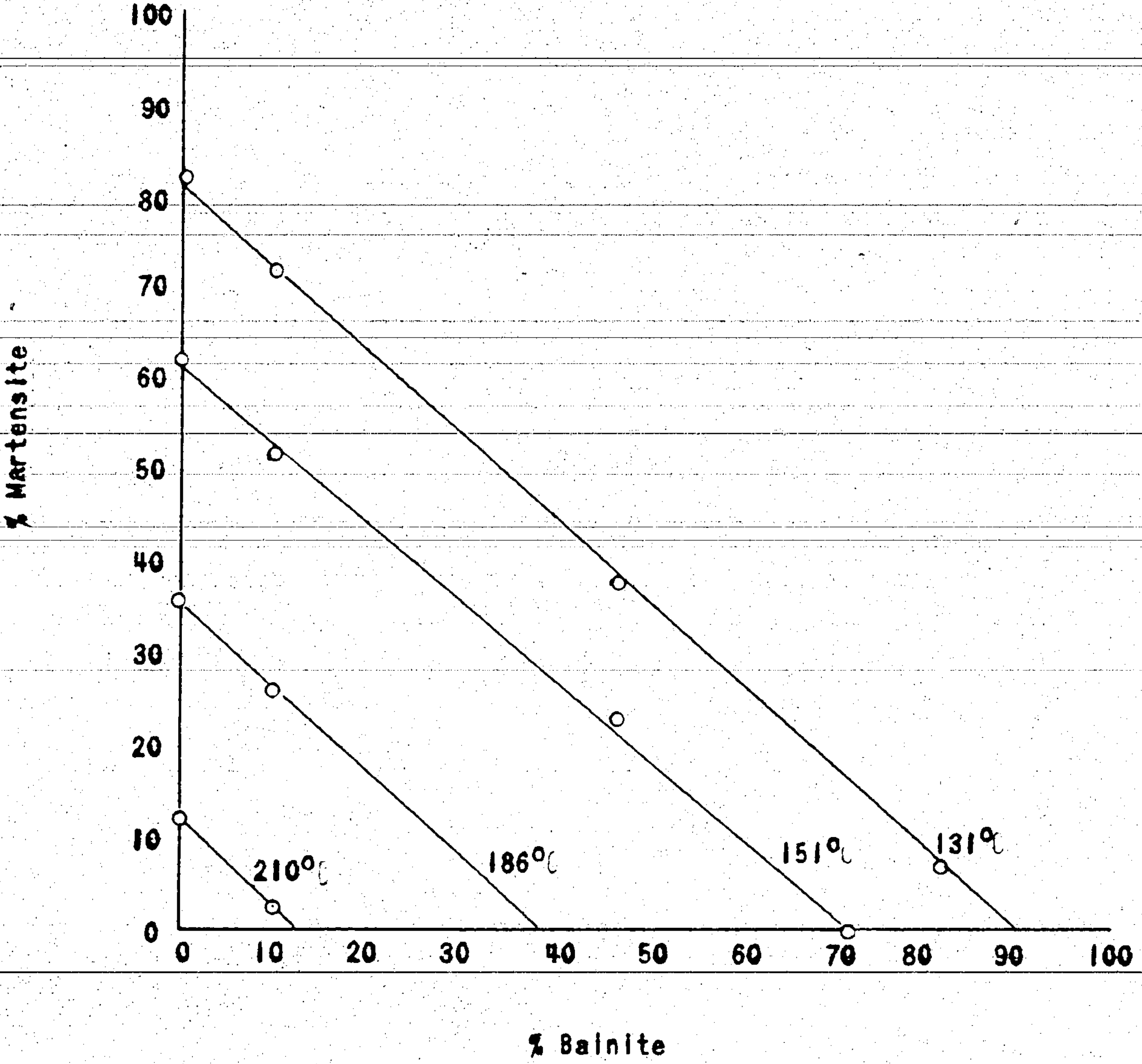


Fig. 25. 0.80% carbon steel transformed isothermally at 242°C to form 82% bainite and then quenched to 131°C. 300X

Fig. 26

Effect of Bainite
on Martensite Formation
0.80% C Steel



Since the temperature for bainite formation in the 0.80% carbon steel was chosen at the M_s temperature, a corresponding temperature was initially chosen for study with the 1.25% carbon steel. A few preliminary determinations indicated that such a study could not be made too easily. The time for formation of the bainite became exceedingly long and the etching characteristics of this bainite were not such as to allow good photometer readings to be made. Nevertheless one or two qualitative determinations were made and the result showed substantial agreement with the above results. The microstructure of this bainite and of a bainite-martensite mixture is shown in Figures 27 and 28. Again it is evident that had the austenite started to form martensite at the original M_s temperature, then complete transformation would have occured on cooling to 25°C. In order to investigate more completely the effect of bainite on the austenite-martensite transformation in the 1.25% carbon steel the bainite was formed at 280°C. Isothermal transformation times of 33, 45, and 65 minutes produced 15%, 37% and 79% bainite respectively as shown in Figures 30, 31, and 32. The austenite accompanying these amounts of bainite was transformed by cooling to various temperatures. The data are plotted in Figure 29 as in the case of the 0.80% carbon steel and it is immediately evident that the same relation holds. The microstructure for the 79% bainite sample cooled to 25°C to transform the remaining austenite are shown in Figure 33. It is evident

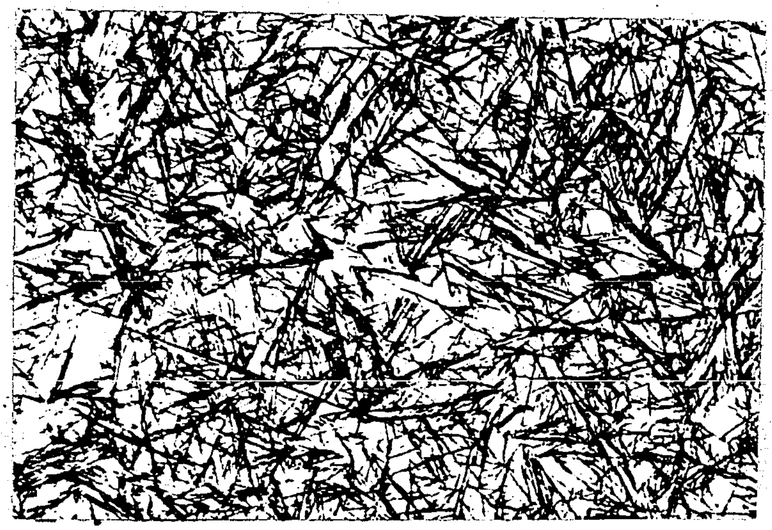


Fig. 27. 1.25% carbon steel isothermally transformed for 20 hours at 150°C. 300X

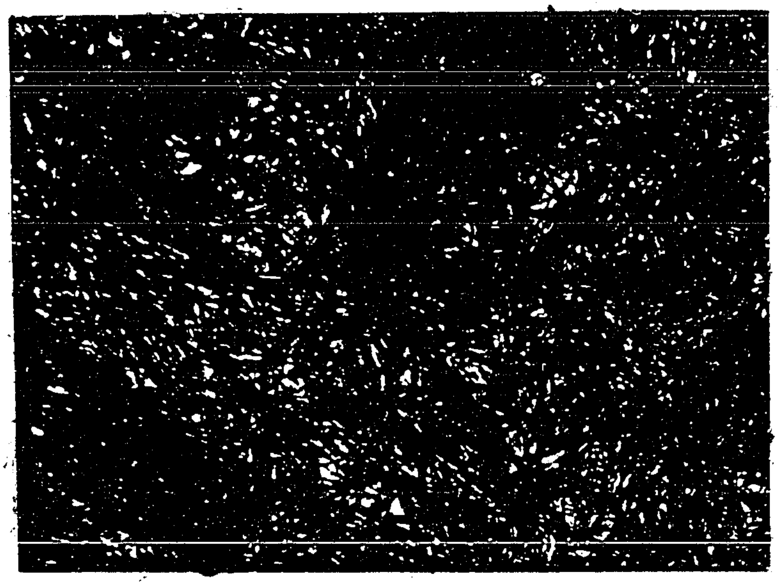
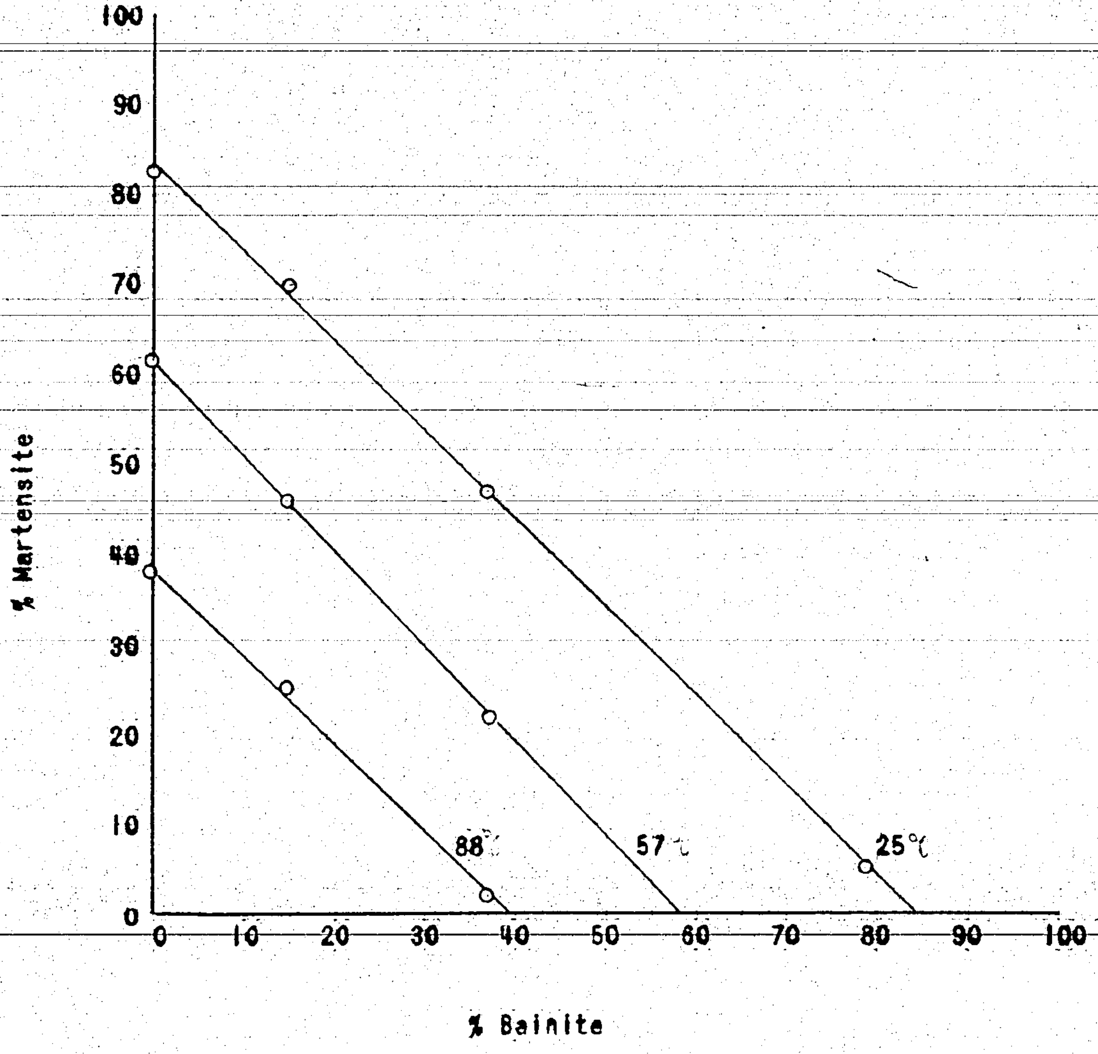


Fig. 28. 1.25% carbon steel isothermally transformed for 20 hours at 150°C and then quenched to 25°C. 300X

Fig. 29
Effect of Bainite
on Martensite Formation
1.25% C Steel



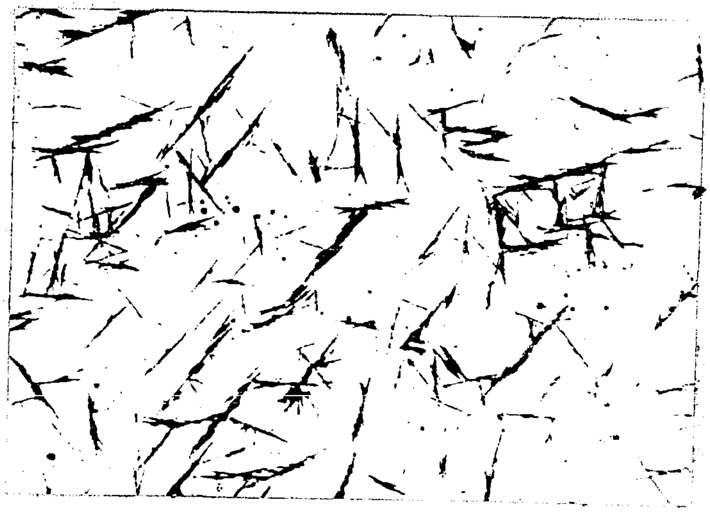


Fig. 30. 1.25% carbon steel isothermally transformed 33 minutes at 280°C. 15% Bainite 300X

Fig. 31. Same as Fig. 30 except 45 minutes. 37% Bainite. 300X

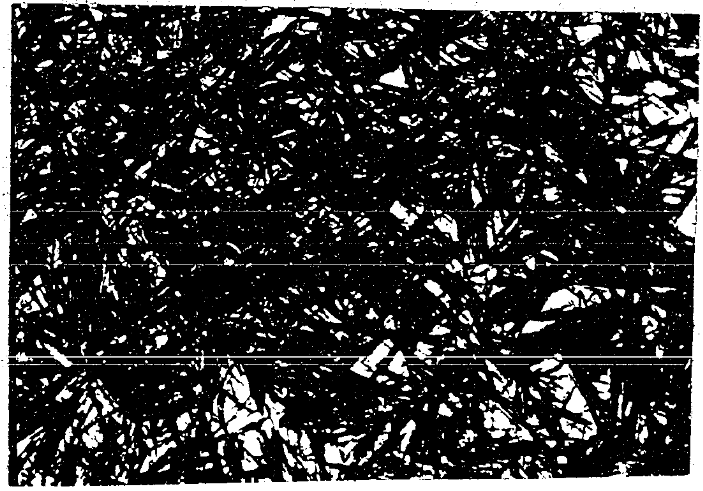


Fig. 32. Same as Fig. 31 except 65 minutes 79% Bainite. 300X

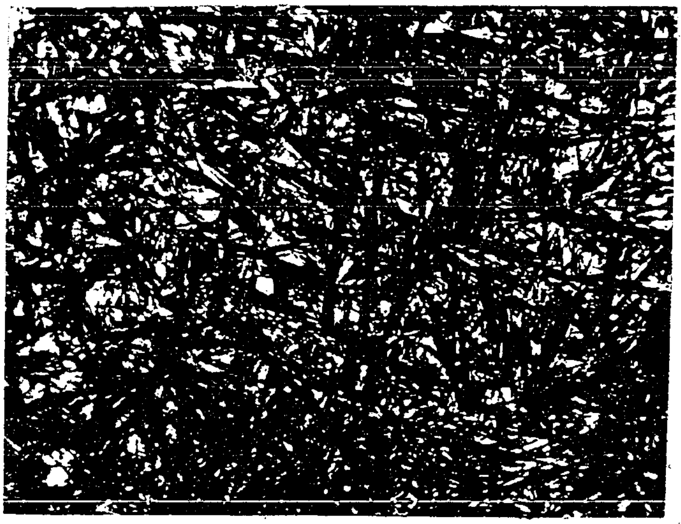


Fig. 33. Sample of structure as in Fig. 33 cooled to 25°C. 300X

that the bainite has greatly repressed the transformation to martensite.

The data for the bainite formation and the effect of various amounts of bainite on the austenite-martensite transformation are given in Tables III and IV.

A careful examination of these mixed structures gave little information upon which any theory explaining the results could be developed. It would seem that the bainite in being some type of supersaturated ferrite was capable of replacing martensite in so far as the course of transformation of the remaining austenite on continuous cooling was concerned. This leaves much to be explained but the data available are not sufficient to allow a more complete analysis. As was mentioned in the theoretical portion of this dissertation, it has been proposed that the carbon rapidly diffuses from the supersaturated ferrite into the surrounding austenite. The M_s temperature of the remaining austenite would then be lowered. Two arguments can be made against such a theory explaining the observed results. In the first place, it is not probable that the M_s would be lowered proportionate to the amount of bainite and, in the second place, the diffusion rates at such low temperatures are so small that little general increase in carbon content could occur nor is the solubility of carbon in austenite known at these low temperatures.

Elmendorf's (29) results on the effect of martensite on the formation of bainite indicated that the martensite accelerated the decomposition of the remaining austenite rather than function as an equivalent amount of bainite. It is interesting to note that in this investigation where the effect of the bainite on the martensite transformation was studied, the bainite did function as an equivalent amount of martensite.

4. The Effect of Holding Times Just Above the M_s Temperature on the M_s Temperature and on the Rate of Formation of Martensite.

Samples of both steels were held just above their respective M_s temperatures for periods of time up until the beginning of isothermal transformation to bainite. From these temperatures and for the various times, samples were quenched to several different temperatures in the martensite range. In all instances the results were the same as if the samples had been cooled directly. These results are in agreement with the results of Zmeskal (27) on a high carbon-high chromium in which holding at room temperature had no effect on the subsequent martensite formation so long as a sufficiently high austenitizing temperature was used to make the steel completely austenitic at room temperature.

5. Effect of Holding Times in the M_s - M_f Temperature Range on the Continuation of the Austenite-Martensite Transformation.

Most of the experimental work pertaining to this variable was confined to the 1.25% carbon steel. Some data however were obtained on the 0.80% carbon steel. The experimental procedure was to quench samples down to a definite temperature in the martensite range and to hold them at this temperature for lengths of time up to that at which transformation to bainite would begin. These samples were then quenched down to some other lower temperature, tempered, and then quenched to room temperatures. The amounts of transformation were then compared to the amounts that were obtained on direct quenching to the lower of the two temperatures. In this manner any affect of the holding time could be measured. The data for both steels are given in Table V.

Holding samples of the 0.80% carbon steel at temperatures above 150°C had no measurable effect on the continuation of the transformation to martensite at any lower temperature. At 150°C samples could be held at temperature up to 2 hours with 64% martensite present. Samples were held 1 hour and 2 hours and then quenched to 130°C where normally 82% of martensite would form on direct cooling. The sample held for 1 hour at 150°C reduced the amount of transformation at 130°C to 78% and the 2 hour sample to 71% martensite. The microstructures of the directly quenched sample and the one held for 2 hours at 150°C are shown in Figures 34 and 35. If the same holding times and temperatures are used but the samples then quenched to87°C which was near

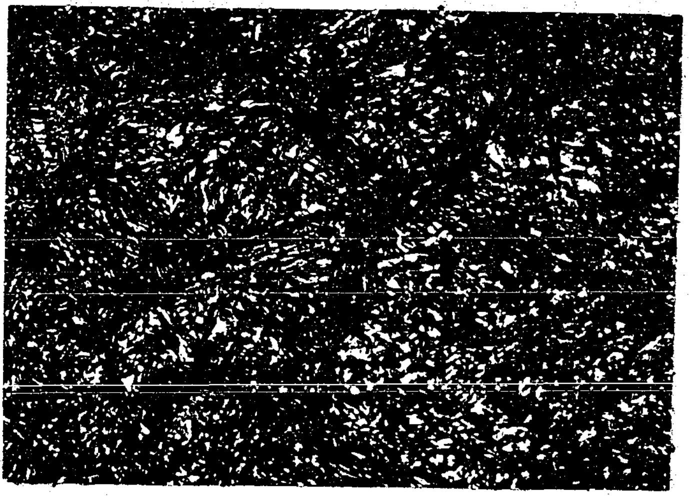


Fig. 34. Martensite formation in 0.80% carbon steel quenched to 131°C. 300X

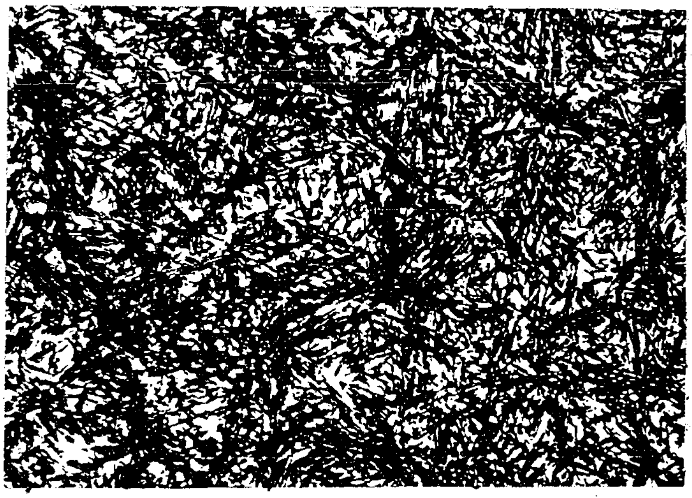


Fig. 35. Same as Fig. 34 except held at 150°C for 2 hours and then quenched to 130°C. 300X

the M_f temperature, then no stabilizing effect was observed. Although these data are not sufficient to show the complete response of this steel to various types of stabilization treatments, certain conclusions and speculations may be made.

Since no stabilization was obtained for temperatures above 150°C, it would seem that these higher temperatures either do not allow enough martensite to be formed to cause stabilization or the higher temperatures do not allow the establishment of the stress distribution to which stabilization phenomena have been attributed. Furthermore since holding at 150°C retards the transformation at 130°C but not at 87°C, the stabilizing effect is one of retarding the transformation. On cooling, transformation is resumed at some lower temperature after which it progresses more rapidly than under direct quenching until transformation is complete at the normal M_f temperature. Furthermore, at 150°C the time of holding is restricted to two hours and to shorter times at higher temperatures which as a variable limits the maximum amount of stabilization that might be expected.

More extensive stabilization studies were made on the 1.25% carbon steel because samples could be held at the various temperatures for longer periods of time without the formation of bainite. The effects of stabilizing at higher temperatures were studied with respect to the amount of transformation at 25°C and -15°C. Samples held at 130°C for 2 hours and at 107°C for as long as 18 hours had no effect on the amount of transformation at these two lower temperatures. These results are in line with those found in studying the 0.80% carbon steel. Since these temperatures are lower than the ones which produced some stabilization in the 0.80% carbon steel, it would seem that a certain amount of martensite is required at the holding temperature before stabilization occurs.

When samples were held at 88°C and then cooled down to 24°C, some stabilization occured. On direct quenching to 24°C, 83% of the austenite transforms to martensite. Holding the sample at 88°C (38% bainite) for 1 minute before quenching down to the lower temperature has no effect on the amount of transformation. The results for holding longer periods of time at 88°C are as follows:

Time at 88°C	% Transformation at 24°C	Increase in % martensite on cooling to 25°C
5 minutes	76%	38%
15 minutes	72%	34%
2 hours	67%	29%
12 hours	76%	38%
24 hours	75%	37%

These data show that there is a definite effect on the transformation if the sample is held at this temperature for only 15 minutes. The effect becomes greater at 2 hours and then decreases after a longer period of time. These determinations were duplicated in order to make sure that intermediate times of holding produced the greatest change in the total amount of martensite formed. Figure 36 shows the microstructure of the directly quenched sample which may be compared to the one held for 2 hours at 88°C before quenching, the latter microstructure being shown in Figure 37.

If the temperature at which the samples are held before quenching is lowered to 57°C, the following results are obtained:

Time at 57°C	% Transformation at 25°C	Increase in % martensite on cooling to 25°
1 minute	79%	18
2.5 minutes	72%	11
15 minutes	61%	0
2 hours	62%	1
4 hours	59%	0
12 hours	60%	0
21 hours	62%	0

The amount of martensite formed on direct quenching was 83% as before. The amount of martensite formed on direct quenching to 57°C was found to be 61%. Thus holding samples at this latter temperature for as short as 15 minutes was sufficient to completely stabilize the remaining austenite with regard to its transformation on cooling to 24°C. Longer holding times than those studied might reduce this stabilizing effect as was the case on holding at 88°C. The microstructure of the 15 minute sample is shown in Figure 38 and may be compared

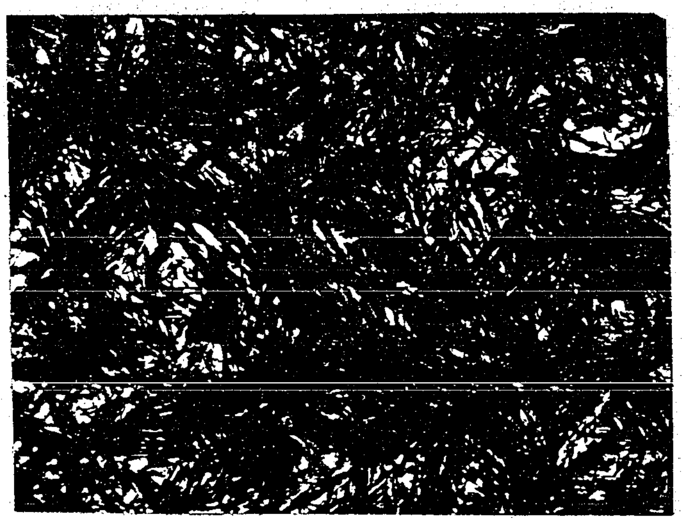


Fig. 36. 1.25% carbon steel quenched to 24°C. 83% martensite. 300X

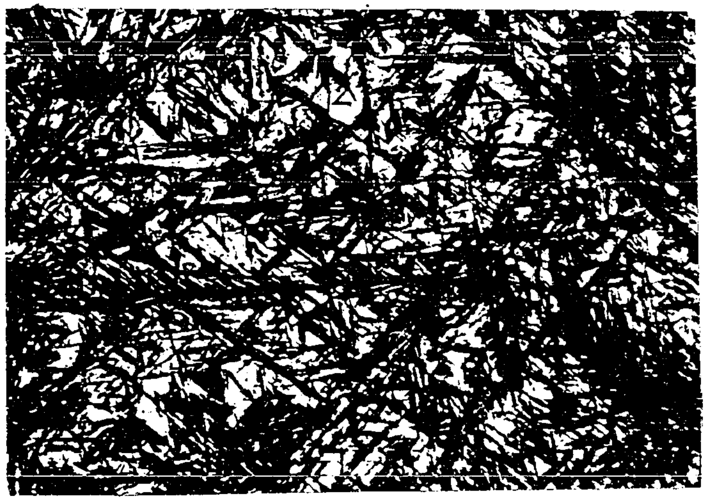


Fig. 37. Same as Fig. 36 except sample held 2 hours at 88°C and then quenched to 24°C. 300X

Fig. 38. 1.25% carbon steel held 15 minutes at 57°C and then quenched to 24°C. 300X

to the directly quenched structure in Figure 37.

In order to continue these studies at lower temperatures an ice-ammonium chloride mixture was used giving a temperature of -15°C. Samples were held as before at 88° and 57°C and in addition several specimens were held at 24°C before further cooling. On direct quenching to -15°C 91% martensite was formed. Holding the samples at 88°C for various lengths of time scarcely affected the amount normally formed at -15°C, 89% transformation being obtained rather than 91%. On holding at 57°C for times up to 12 hours, the amount of transformation was reduced to 85% on cooling to -15°C. Since this holding temperature had completely stabilized the untransformed austenite on cooling to 24°C, the transformation to martensite must have again started at some temperature below 24°C. To varify this a sample was held for 105 minutes at 56°C and then quenched to 5°C. The sample showed a total transformation of 72% martensite which indicates that the transformation had again started at some temperature between 5° and 24°C and must then proceed at an accelerated rate giving 85% transformation at -15°C.

A series of samples was then held at 24°C before cooling down to -15°C in order to determine the room temperature stabilization. The following results were obtained:

Time at 24°C	% Transformation at-15°C	Increase in % martensite on cooling to -15°C
5 minutes	91%	8
15 minutes	87%	4
105 minutes	83%	0
12 hours	82%	0

15 minutes at room temperature were thus sufficient to have some stabilizing effect on cooling to -15°C and 105 minutes were sufficient to completely stabilize the austenite on cooling through this temperature range.

These results on austenite stabilization as a result of holding martensite-austenite mixtures at various temperatures bring up a number of facts which may be discussed in a general manner. Based upon the results obtained from a study of these two steels, it seems that a definite amount of martensite must be present before holding at any temperature will stabilize the transformation of the remaining austenite. If the temperature at which sufficient austenite can be obtained is high enough, there appears to be an optimum time which will produce the maximum stabilization. On the basis that stabilization is due to a stress redistribution following some initial martensite formation, a definite time seems to be required to establish such stress condition. At these higher temperatures some tempering may occur in time which further changes the stress distribution and decreases the stabilization of the austenite. It is proposed that longer times would cause a decrease in the stabilization of the austenite of the 0.80% carbon steel held at 150°C if it were not for the fact that holding times are restricted to two hours due to the beginning of formation of bainite. The 1.25% carbon steel held at 57°C did not show the decrease in stabilizing tendency at the end of 21 hours. It seems possible that the lower temperature would not allow the tempering to occur that had taken place at the higher temperature samples and thus no change in the stabilization tendencies would be expected.

6. The Effect of Time at the Austenitizing Temperature on the M_s Temperature and on the Rate of Martensite Formation.

Since most of the work reported in this dissertation was confined to decomposition studies of homogeneous austenite, few studies were made on the effect of time at the austenitizing temperature. In order to allow rapid heating to the austenitizing temperature, samples of the 0.80% carbon steel were cut 0.013" thick. Heating only two minutes at 1050°C was sufficient to give the same amount and uniformity of martensite at the M_s temperature as longer austenitizing temperatures. The effect of time at the lowest austenitizing temperature, 735°C, should be most pronounced since the diffusion rates would be lowest at this temperature. Samples were held at this temperature for 15', 30', and 45' and then quenched to 210°C. For each time the same amount of transformation (25%)

was obtained showing that at this temperature 15 minutes was sufficient to produce homogeneous austenite from the original normalized structures.

7. The Effect of Varying Amounts of Martensite on the Transformation of Austenite Retained After Tempering.

It was not intended to study this variable in this investigation but a few determinations were made, the results of which may be at least qualitatively stated. The procedure was to quench the austenitized sample to some temperature below the M_s temperature, temper for 5 or 6 seconds at 280°C, cool again to the initial quenching temperature, temper again and then quench. The results indicate that the austenite held at the tempering temperature for only 5 or 6 seconds raises slightly the temperature for the continuation of transformation on again cooling. For example an 0.80% carbon steel sample was quenched to 151°C, tempered, and again cooled to 151°C before again being tempered and quenched to room temperature. Examination of the sample shows that on the second cooling to 151°C 5% additional martensite had formed.

CONCLUSIONS

The effects of several variables on the austenite-bainite and austenite-martensite transformations have been investigated for steels of two different carbon contents. The data permit the following conclusions to be drawn:

1. For a plain carbon steel of eutectoid composition, the M_s temperature increases with austenitizing temperature up to an austenitizing temperature of 815°C and is thereafter independent of the austenitizing temperature. On increasing the austenitizing temperature from 735°C to 815°C, the M_s temperature increases from 228°C to 242°C. The initial formation of martensite with decrease in temperature is greater for the lower austenitizing temperatures.

2. For a plain carbon steel of eutectoid composition, the austenite remaining after quenching to various temperatures below the M_s temperature will transform isothermally to bainite after a definite lag time. In the presence of different amounts of martensite formed at the same temperature by using different austenitizing temperatures, the beginning of the bainite formation occurs at about the same time and continues to form at a rate relatively independent of the initial amounts of martensite. In this steel, small amounts of martensite just below the M_s temperature are capable of accelerating the beginning of transformation to bainite.

3. For both the 0.80% and 1.25% carbon steels, partial isothermal transformation to bainite lowers the M_s temperature for the remaining austenite to a temperature which would have allowed an amount of martensite to form equal to the amount of bainite present before continuing the cooling.

4. For both the 0.80% and 1.25% carbon steels, holding samples just above the respective M_s temperatures for times up to those allowing the bainite to form has no affect on the normal transformation of the austenite to bainite.

5. For both the 0.80% and 1.25% carbon steels, the austenite remaining after partial transformation to martensite may be stabilized with regard to its further transformation to martensite. It seems that a definite amount of martensite must be present if stabilization is to occur. At any temperature, the effect of stabilization increases with time of holding. If the temperature is sufficiently high, the stabilization goes through a maximum and then decreases probably due to the tempering of the martensite.

6. If the time at temperature is sufficiently long to form homogeneous austenite, longer times do not affect the austenite-bainite and austenite-martensite transformations.

7. Tempering mixtures of martensite and austenite for 5 or 6 seconds above the M_s temperature does not materially alter the austenite. The transformation of the austenite to martensite again continues on cooling to the original temperature at which the austenite-martensite had been formed.

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TABLES

Table I

Isothermal Transformation Data

Sample No.	Temp. °C	Time	Photometer Reading	% Transformation
Austenitizing Temp. 1050°C				
242	242	10 sec.	95.5	1
243	242	3 min.	95	1
244	242	5 min	95	1
245	242	10 min.	88	9
246	243	20 min.	55	47
247	243	30 min.	25	82
248	242	45 min.	11	97
249	242	65 min.	9	100
Austenitizing Temp., 760°C				
250	242	10 sec.	96	0
251	242	5 min.	95.5	1
252	242	10 min.	92	5
253	242	20 min.	70	30
254	242	30 min.	30	76
255	242	46 min.	12	96
Austenitizing Temp., 1050°C				
219	226	10 sec.	96	7
222	226	3 min.	89	8
223	226	5 min.	96	7
292	227	7 min.	90.5	6.3
296	227	8 min.	90	7
335	226	10 min.	89	8
333	226	20 min.	72	28
334	227	40 min.	26	80.5
295	227	63 min.	12	97
Austenitizing Temp., 760°C				
345	227	1 min.	94	3
343	226	10 min.	93.5	3
344	226	20 min.	86	11.5
341	226	40 min.	33	72.5
347	226	80 min.	14	94
Austenitizing Temp., 1050°C				
277	210	10 sec.	85	12.5
278	210	5 min.	86	11.5

Sample No.	Temp. °C	Time	Photometer Reading	% Transformation
283	210	8 min.	84.5	13
279	210	10 min.	84	14
280	210	15 min.	78	21
259	210	20 min.	72	28
260	210	40 min.	46	58
261	210	64 min.	22	85
262	210	124 min.	11	97
Austenitizing Temp., 760°C				
266	210	30 sec.	80.0	18
267	210	5 min.	81	17
268	210	10 min.	80.5	18
269	210	15 min.	75	24
270	210	20 min.	63	38
271	210	40 min.	34	71
272	210	60 min.	21	87
273	210	120 min.	12	97
Austenitizing Temp., 735°C				
274	210	1 min.	75	25
Austenitizing Temp., 815°C				
348	210	1 min.	87	10
Austenitizing Temp., 1050°C				
300	186	1 min.	65	36
331	186	5 min.	64	37
352	186	15 min.	64	37
332	185	20 min.	62	39
342	186	25 min.	64	37
354	185	30 min.	62	39
302	187	45 min.	52	51
303	186	65 min.	43	61
304	186	120 min.	33	72
305	186	240 min.	25	82
Austenitizing Temp., 760°C				
310	186	1 min.	55	47
320	187	20 min.	57	45
311	186	30 min.	54	48
312	187	45 min.	42	62
314	186	122 min.	25	82
315	187	240 min.	16	92

Sample No.	Temp. °C	Time	Photometer Reading	% Transformation
		Austenitizing Temp., 735°C		
317	186	1 min.	48	55
		Austenitizing Temp., 815°C		
346	186	1 min.	64	37
		Austenitizing Temp., 1050°C		
357	151	1 min.	42	62
360	151	60 min.	41	63
378	152	120 min.	39	66
363	151	250 min.	36	69
361	151	600 min.	28	78
372	151	1440 min.	25	82
		Austenitizing Temp., 760°C		
365	151	1 min.	33	73
367	151	60 min.	34	71
368	151	120 min.	33	73
370	151	250 min.	31	75
371	151	400 min.	26	80
373	151	1860 min.	21	86
		Austenitizing Temp., 735°C		
366	151	1 min.	25	82
		Austenitizing Temp., 815°C		
369	151	1 min.	42	62
		Austenitizing Temp., 1050°C		
386	131	1 min.	24	82
392	130	560 min.	21	86
390	130	1200 min.	20	88
396	129	2790 min.	18	90
404	130	4200 min.	17	91
		Austenitizing Temp., 760°C		
383	131	1 min.	21	86
393	130	565 min;	19	88
391	130	1140 min.	17	91
397	129	2640 min.	15	93
405	130	4130 min.	14	94

Sample No.	Temp. °C	Time	Photometer Reading	% Transformation
		Austenitizing Temp., 735°C		
384	131	1 min.	14	94
		Austenitizing Temp., 815°C		
385	131	1 min.	26	80

Table II

Martensite Formation on Direct Quenching

1.25% Carbon Steel

Sample No.	Temp. °C	Time	Photometer Reading	% Martensite
		Austenitizing Temp., 1050°C		
377	140	1 min.	96	1
---	135			M_s
407	107	1 min.	83	15
423	87	1 min.	63	38
468	57	1 min.	42	62
459	24	1 min.	24	83
465	-15	2 min.	17	91

0.80% Carbon Steel

Sample No.	Temp. °C	Time	Photometer Reading	% Martensite
		Austenitizing Temp., 1050°C		
413	107	1 min.	20	88
421	87	1 min.	18	92
		Austenitizing Temp., 760°C		
414	107	1 min.	16	92
419	87	1 min.	12	97
		Austenitizing Temp., 735°C		
415	108	1 min.	11	98

Table III

Bainite Formation Data

Sample No.	Temp. °C	Time	Photometer Reading	% Bainite
		0.80% C		
245	242	10 min.	88	10
246	242	20 min.	55	47
---	242	25 min.	33	72
247	242	30 min.	25	82
		1.25% C		
394	150	90 min.		Approx. 3
398	150	193 min.		Approx. 5
411	150	780 min.		Approx. 15
417	150	1230 min.		----
		1.25% C		
430	280	33 min.	83	15
420	280	45 min.	64	37
434	280	65 min.	27	79

Table IV

Data on Effect of Bainite on Martensite Formation

0.80% C

Austenitizing Temperature 1050°C

Sample No.	% Bainite at 242°C	Martensite Trans.Temp.	Total Trans. %	% Martensite
277	0	210	12.5	12.5
286	10	210	12.5	3.5
300	0	186	36	36
306	10	186	36	26
356	47	186	57	0
357	0	151	62	62
358	10	151	62	52
359	47	151	70	23
364	82	151	83	0
379	72	151	72	0
386	0	131	82	82
388	10	131	82	72
389	47	131	85	38
387	82	131	89	7

1.25% C

Austenitizing Temperature 1050°C

Sample No.	% Bainite at 150°C	Martensite Trans.Temp.	Total Trans. %	% Martensite
395	3	24	83	80
399	5	24	83	78
412	15	24	87	57
418	25	--	86	--
	% Bainite at 280°C			
423	0	87	38	38
436	15	87	40	25
428	37	87	39	2
468	0	57	62	62
438	15	55	61	46
439	37	55	59	22
459	0	24	83	83
433	15	25	85	70
429	37	25	84	47
432	79	25	84	5

Table V

Austenite Stabilization Data

All Austenitizing Temperatures, 1050°C

Sample No.	Stabilizing Temp., °C	Stabilizing Time., Min.	Quenching Temp.	Normal %Trans.	After Stabilization % Trans.
		0.80% C			
400	150	65	130	82	78
401	150	25	130	82	71
		1.25% C			
482	56	1	25	83	79
489	56	2.5	25	83	72
477	56	15	25	83	62
471	56	15	24	83	61
479	55	120	24	83	62
460	57	240	25	83	59
461	57	720	25	83	59
484	56	720	25	83	60
442	55	1260	25	83	62
483	88	1	24	83	84
476	88	5	24	83	76
478	88	15	24	83	72
470	88	15	24	83	75
480	88	120	24	83	67
488	88	120	25	83	70
462	88	720	25	83	76
474	88	1440	25	83	75
410	107	620	25	83	84
416	107	1080	25	83	
408	310	120	25	83	84
492	56	105	5	--	72
481	25	5	-15	91	91
490	25	15	-15	91	87
491	25	105	-15	91	83
464	25	720	-15	91	82
493	56	105	-15	91	84
486	56	720	-15	91	86
467	57	900	-15	91	86
494	88	120	-15	91	90
487	88	720	-15	91	88
466	88	900	-15	91	89