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I hereby recommend that the thesis prepared under my supervision by Earle Raymond Saunders *entitled* A Study of Martensite Formation

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

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A STUDY OF MARTENSITE FORMATION

A dissertation submitted to the
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requirements for the degree of
DOCTOR OF PHILOSOPHY
1941
by

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Introductory Remarks

One of the most important and fundamental problems which at present confronts the physical metallurgist is the nature and mechanism of the reactions occurring in quenched steels. Steels quenched from the austenitic field may result in one or in a combination of several different structures, depending upon the severity of the quench employed. Rapid cooling rates, as produced by a water quench, result in the formation of a particularly hard, brittle structure known as martensite.

The study of martensite formation in steels is but a specialized phase of the investigations pertaining to the decomposition rates of austenite. Austenite is a solid solution of carbon in γ-iron. On slowly cooling austenite, it will first reject a pro-eutectoid phase, and then, at some temperature lower than Ac_1 (723°C for plain carbon steels) the remaining austenite will transform to the eutectoid structure, pearlite. The formation of pearlite results from a rhythmic process producing alternate layers of ferrite and cementite. In order to produce cementite in this eutectoid, carbon diffusion must take place--the carbon atoms having been as far apart as possible while dissolved in the γ lattice. Fundamentally, this austenite decomposition is concerned with an allotropic change from γ to α iron and pre-

cipitation of the dissolved carbon. Since diffusion processes require time, increasing the cooling rates results in progressively finer laminations of pearlite. The rapid cooling rates produced by an oil quench when dealing with plain carbon steels results in a characteristic microstructure designated troostite. This troostite is, however, also classified as a member of the lamellar family. Finally, drastic quenching agents, such as water, yield cooling rates so rapid that carbide precipitation is completely suppressed, the carbon remaining in a state of atomic dispersion in the ferrite produced during the allotropic transformation. Thus the reaction to be investigated in this research consists of the transition from a solid solution of carbon in γ-iron to a solid solution of carbon in α-iron or some intermediate structural forms.

In order to separate the influence of temperature and time in the study of austenite transformations, the progress of the decomposition is usually determined at a series of constant temperature levels. This is necessitated by the fact that the rapidity of the reactions involved in plain carbon steels makes direct investigation of transformation during cooling extremely difficult. Isothermal transformation at any given temperature level results in the formation of a uniform product, whereas transformation during continuous cooling produces a mixture of products as the decomposition

proceeds over a range of temperatures. Each product formed during the cooling process may be regarded as the result of transformation at a givem temperature, and is substantially the same as that produced isothermally at the same temperature. Consequently, the transformation produced during continuous cooling may be considered to be the result of a series of isothermal decompositions. In this way, the isothermal investigation of austenite affords a convenient method for studying the nature of austenite decomposition. Since the instigation of research by means of isothermal investigations, this method has attained tremendous importance per se because of its industrial application in austempering.

There are several experimental paths which can be followed in studying the nature and rate of austenite decomposition at constant sub-critical temperatures. In the first place, there is a volume change accompanying the transformation of austenite. Since γ-iron consists of a face-centered lattice, whereas α-iron present in each of the decomposition products is of the body-centered type, there must necessarily be a volume increase during the reaction. Martensite is the least dense of the decomposition products, the expansion due to complete transformation being approximately two per cent. Experimental difficulties involved in measuring volume changes accurately while the sample is maintained in the quenching medium have led to the simplification of the method

by measuring length changes. Such dilatometric investigations are subject to criticism, for volume changes are not necessarily proportional to linear changes. However, by selecting specimens for study that have a high ratio of length to cross sectional area, such a method does yield valuable qualitative data. At least, dilatometric investigations do indicate the time necessary for the beginning and end of transformation, and consequently have proven to be of considerable worth.

Secondly, since γ-iron is non-magnetic while α-iron is magnetic, the problem of austenite decomposition lends itself to magnetic analysis. Up to the present time, the inherent difficulties in experimental magnetic work plus the difficulty of proper interpretation of magnetic data have prevented general application of this method although a certain amount of valuable information has been obtained. It seems probable that, in the future, magnetic methods will assume more importance in the solution of the problem of martensite formation.

A third method for study which has been rapidly gaining favor is metallographic investigation. In this procedure, the reaction is permitted to progress at a given isotherm for a measured time interval, then the specimen is quenched abruptly to room temperature to prevent further transformation. On subsequent polishing and proper etching of the sam-

ple, the transformed structure can be distinguished and the per cent decomposition evaluated. By repeating this process with a series of samples maintained at the isotherm for increasing lengths of time, the rate of reaction may be determined. The metallographic method is considered by many investigators to be the most accurate means available for following isothermal transformations. The main disadvantage in such studies is the tediousness of preparing and examining a large number of samples. Such a drawback is, of course, of no consequence from the theoretical viewpoint, but the factor of time is of sufficient importance to prevent general acceptance of microscopic examination.

There are numerous other methods available for experimental work, such as:

1- x-ray analysis
2- resistance changes
3- acoustic measurements

Such methods have not as yet attained sufficient importance to be considered in detail. In general, all studies on the decomposition of austenite to martensite may be classified as metallographic, magnetic, and dilatometric.

Rate of Martensite Formation

The subject of the transformation of austenite to martensite has occupied a prominent place in research during the past twenty years. Le Chatelier (1) is considered to have been the first investigator to suggest the possibility of a hardening transformation in steels. By rapidly cooling plain carbon steels, he discovered that austenitic decomposition could be prevented in the high temperature region although he failed to locate a reaction at lower temperatures. Chevenard (2) succeeded in showing the presence of a hardening transformation at a low temperature. The temperature at which transformation occurs at a maximum velocity in the upper region was designated the Ar' point and the temperature at which transformation occurs in the lower range- Ar". Portevin and Garvin (3) are among the first investigators to determine the temperature at which martensite formation occurs in steels. The data obtained as a result of thermal analysis at various cooling rates serves to indicate that martensite structures are obtained as a result of transformation below 300°C. Lewis (4) conducted experiments on martensite formation in 0.80% plain carbon steels, using both magnetic and dilatometric methods. Results indicated that specimens could be quenched rapidly enough to 232°C to prevent austenite transformation. Further cooling from this temperature causes the formation of martensite; final hardness of the

piece is substantially independent of the rate of cooling. At temperatures below 232°C, austenite decomposition appeared to be very rapid and the product was martensite. At temperatures above 232°C, austenite remained constant for a considerable period of time--transformation yielding a structure microscopically similar to martensite, but of low hardness.

S-Curve Theory---Pioneering work on isothermal investigations of austenite decomposition was conducted by Davenport and Bain (5), using both dilatometric and metallographic methods. The procedure employed in the metallographic method involved permitting transformation to occur for a measured time interval and then preventing further transformation by a rapid quench to room temperature. The martensite produced on the final quench represented the austenite unchanged during the time at the isotherm. Obviously such a method can not be applied directly to the study of martensite formation itself. Consequently, for study of the products obtained at the lower temperatures, the dilatometric method only was used. It was unfortunate that the admittedly least accurate method was the only means available for study of the rapid austenite-to-martensite reaction.

The result of these important investigations of Davenport and Bain was the now famous S-curve theory for transformation of austenite. This theory postulates that at any given isotherm to which a sample is quenched there is a definite

time interval during which the specimen remains 100 per cent austenitic. After this period has been exceeded, the transformation begins, and proceeds isothermally to completion. At the lower temperatures employed, the lag time prior to decomposition becomes progressively smaller. Similarly, the time required for complete decomposition decreases rapidly at temperatures below 200°C. Figure 1 illustrates a typical S-curve for transformation of austenite--representing the results obtained on a series of isothermal runs.

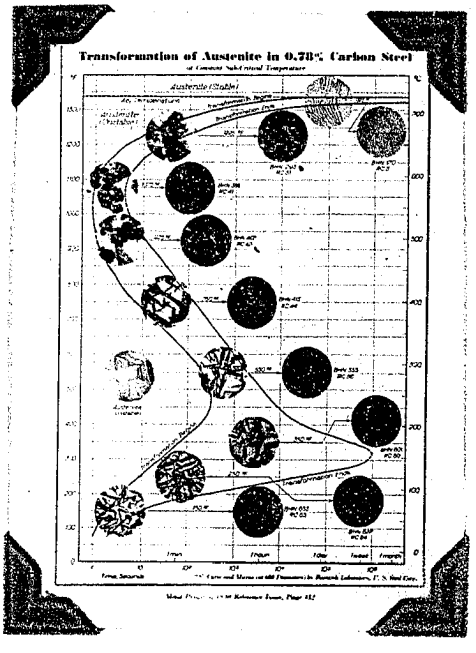


Figure 1

At temperatures below 200°C, conversion to martensite occurs. If the temperature is maintained at some point between 300°C and 200°C, a hard product, microscopically similar to martensite, is produced. This product was designated martensite-troostite by early investigators, and has since become known as bainite. The temperature which serves as a line of division between the formation of martensite and bainite is a function of the chemical composition of the steel, and represents the Ar'' temperature.

Bain and Davenport explained the increased rate of reaction at successively lower temperatures than 200°C as the result of two separate factors. The softer product of transformation above the maximum reaction time in this low temperature range (i.e. bainite) lacks the hardness and strength to exert during its expansion a very great outward force. The harder martensite formed at lower temperatures is capable of producing great forces as a consequence of the expansion occurring during its formation. The negative pressure so produced has an auto-catalytic effect upon the conversion of the remaining austenite. The second factor presented reasons that the time-consuming element in transformation is the precipitation of carbide -- or rather, the diffusion of carbon which necessarily precedes carbide precipitation. Since martensite is a structure very similar to a solid solution, its formation is not dependent upon carbon diffusion, but merely upon

the atomic rearrangement accompanying an allotropic change from γ- to α-iron. Accordingly, martensite formation may proceed at very rapid rates.

As a direct consequence of this original research on isothermal decomposition, a tremendous amount of material has been published along parallel lines. Continued investigation by Bain and Davenport has resulted in the publication of a series of S-curves, illustrating the effect of alloying elements and grain size upon the shape and position of the curve. Numerous other investigators have also examined the transformation of austenite in various alloy steels,--in all cases obtaining reaction curves possessing similar characteristics to the curves published by Bain and Davenport.

Despite the amount of research resulting from S-curve investigations, little additional light has been shed upon the rate of martensite formation. The most important aspect of the S-curve from the practical viewpoint is the position of the so-called'nose' of the curve. In order to produce a martensitic structure, it is necessary to cool the specimen at a rate sufficiently rapid to prevent transformation at a higher temperature. Thus, any factors which cause the 'nose' of the curve to be shifted to the right, along the time axis, increase the hardenability of the steel. The minimum lag time in this high temperature range is the criterion for the critical cooling rate necessary for hardening. Consequently,

the aim of most investigators has been to confine their studies to the rate of reaction at the Ar′ temperature. Johnson and Mehl (6) have published an equation which expresses the rate of austenite decomposition in this higher temperature field. Similar work has been conducted by Austin (7). Since the austenite transformation at these temperatures takes place as the result of nucleation at the grain boundaries and radial growth toward the center of the parent austenitic grain, whereas martensite formation obviously takes place by an entirely different mechanism, these investigations have not added to the knowledge of decomposition below the Ar″ temperature. Original S-curve work and all subsequent investigations have merely shown that the reaction of austenite to martensite proceeds with increasing rapidity at successively lower temperatures.

Martensite as a Product of Cooling

At the present time, there exists a theory of martensite formation which is directly contradictory to the S-curve interpretation. Where Davenport and Bain may well be considered the 'fathers' of the S-curve work, Carpenter and Robertson (8) assume a similar position in the advancement of the theory that martensite formation occurs only during a cooling process. Robertson (9) states that for a steel of a given composition, the Ar″ temperature is the same for a variety of conditions. If we consider cooling velocities sufficient to pre-

vent Ar' transformation, the temperature at which martensite forms is independent of the cooling rate. Wever and Engel (10), and Wever and Ross (11) have experimentally proven the Ar" independence of cooling rates. Matsushita (12) was apparently the first to discover that continuous formation of martensite requires continuous cooling. Specimens were quenched from the austenitic field into a water bath until martensite formation commenced, withdrawn into air for varying time intervals, and finally quenched to room temperature. The austenite decomposition was found to be rapid during the initial quench, so slow as to be immeasurable during the time interval in air, and very rapid again on the final quench.

Tamman and Scheil (13), using a dilatometric method, discovered in their studies that austenite retained at room temperature remains in metastable equilibrium due to its slow decomposition rate,--further cooling resulting in rapid transformation. Andrew,Fisher, and Robertson (14) confirmed these results that rapid decomposition of austenite occurred during cooling with very slow transformation along an isotherm. Forster and Scheil (15) measured acoustically the formation of martensite in 29% nickel steels below room temperatures. Martensite formation began at -31°C and continued during cooling. When the cooling process was interrupted, the transformation rate decreased rapidly; on the resumption of cooling, austenite decomposition proceeded again.

The results of all these investigators indicate that in conducting isothermal transformations below the Ar″ temperature, martensitic formation takes place during the cooling to the isotherm. Additional austenite decomposition occurs at the isotherm, but at a much slower rate. The amount of martensite formed on cooling is dependent upon the difference between the Ar″ temperature and the isothermal temperature, but is independent of the cooling rate. The previous discussion of the S-curve theory postulated that the temperature of martensite formation may be lowered by rapid cooling rates, and that a definite, though small, lag time exists at an isotherm prior to any transformation.

American metallurgists generally accepted the S-curve as a true picture of austenitic transformation at all isotherms, while the theory advanced by Carpenter and Robertson received favor in Europe for the decomposition in the range where martensite formation occurred. Special consideration should be given the recent work of Greninger and Troiano (16). Their investigation has served to bring the discrepancies between the two divergent theories into a prominent position--stimulating research which will definitely settle the problem. A metallographic method was developed to study the formation of martensite, and, in general, the interpretation Carpenter and Robertson have given to this reaction was confirmed. Martensite formation was found to commence as soon as the specimen temperature attained the upper limit (Ar″) of the martensitic range, and

to continue during cooling to the isotherm. As the sample was held at the constant temperature, further transformation took place after a measurable time interval. The rate of isothermal decomposition decreased with lowering of the temperature of the quenching bath.

The difference between these two ideas of martensite formation may be attributed to the inaccuracy of the experimental data acquired in the original S-curve work. The presence of a definite lag time of a few seconds might be due to the fact that the size of specimen employed prevented rapid quenching into the martensite region. The observation that the time for completion of the reaction decreased with temperature according to the S-curve could be explained on the basis that measurements were actually being made of the martensite formation during the process of cooling. The slow or immeasurable rate of reaction prior to true isothermal decomposition was taken as an indication of the completion of the transformation. Bain and Davenport (5) have admitted lack of faith in the accuracy of their low temperature measurements. Hoyt (7) claims dilatometric data on martensite formation is completely unreliable. Improved dilatometric apparatus has been applied to martensite formation, but in principle it is subject to the same criticism as the cruder instruments first used. Parke and Herzig (8), using a dilatometer for the study of molybdenum steels, have reported a

two stage isothermal transformation--at 240°C the initial reaction commencing in 1/32 of a second and ending in 1 second. It appears more likely, however, that the first reaction actually occurs during cooling, and the second reaction represents true isothermal decomposition. Austin and Rickett (19) have also suggested the possibility of a two stage reaction, but formal proof of such a process is lacking.

In conclusion, it seems that experimental evidence indicates that rapid martensite formation occurs during cooling below the Ar″ temperature, and that austenite decomposition proceeds slowly along an isotherm in this range. The S-curve theory of transformation, however, can not be discarded as yet. Recent work by Vilella (20), using the same steels as Greninger and Troiano, has shown martensite formation to occur according to the S-curve. Obviously, no satisfactory explanation of the reaction, austenite to martensite, can be developed until additional experimental data has served to definitely establish the mechanism of the transformation.

The Nature of Martensite

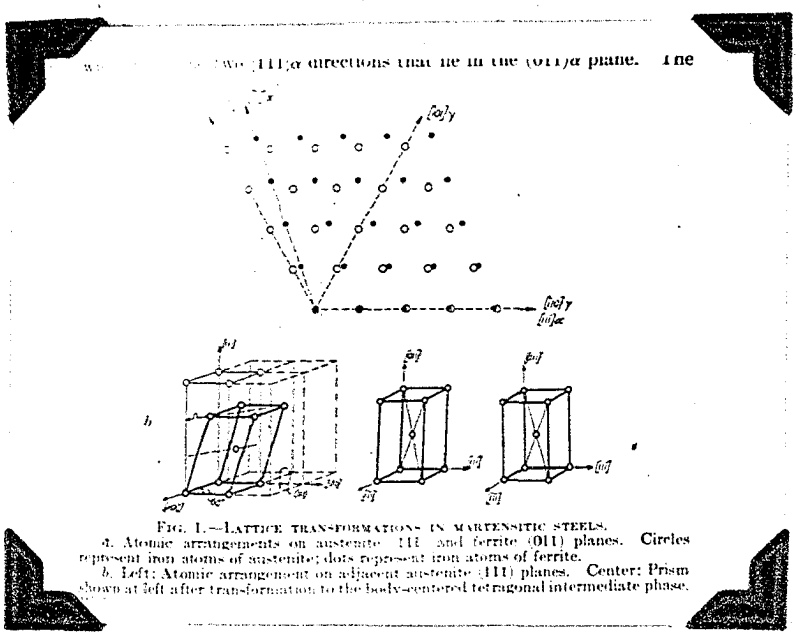
The foregoing discussion has dealt with the rate of martensite formation without consideration of the nature of this structure, beyond describing it as a solid solution of carbon in α-iron. A wealth of material has been published on martensite, leading to several theories regarding the reason for its extraordinary hardness. The following section will attempt to review the more important studies that have been conducted on the martensite structure.

X-ray evidence is fairly conclusive that martensite is composed of carbon dissolved in body-centered tetragonal or body-centered cubic iron. On the assumption that the solubility of carbon in the tetragonal iron closely approximates the solubility of carbon in ferrite (i.e.-less than 0.01%), there must be a tremendous degree of supersaturation in steels of eutectoid composition. Bain (21) was the first investigator to suggest the possibility of tetragonal martensite,--a suggestion experimentally confirmed by Fink and Campbell (22). Since the lattice of austenite may be regarded as a tetragonal body-centered arrangement with the c/a ratio 1.4, Bain suggested that the transformation from austenite to martensite consisted of the shortening of the c axis, and the lengthening of the a axis. Later investigations by Kurdjumow and Sachs (23) showed that the translation proceeded in a different manner. Figure 2 indicates the similarity in spacing of the atoms on the $(111)_\delta$ plane and the

atoms on the (011)α plane. These two conjugate planes may be superimposed in six ways by bringing into co-incidence each of the three [110]γ directions, which occur in the (111) γ plane, with one of the two [111]α directions that lie in the (011)γ plane. Since there are four planes constituting the form {111}γ, there are twenty-four transformations required. The formation of martensite from austenite may accordingly be summed up as:

$$(111)\gamma \parallel (011)\alpha$$

$$[\bar{1}01]\gamma \parallel [1\bar{1}1]\alpha$$



...two {111}α directions that lie in the (011)α plane. The

FIG. 1.—LATTICE TRANSFORMATIONS IN MARTENSITIC STEELS.
a. Atomic arrangements on austenite (111) and ferrite (011) planes. Circles represent iron atoms of austenite; dots represent iron atoms of ferrite.
b. Left: Atomic arrangement on adjacent austenite (111) planes. Center: Prism shown at left after transformation to the body-centered tetragonal intermediate phase.

Figure 2

The alteration may be considered to be a shearing movement of γ atoms in the $[\bar{1}10]\gamma$ direction, in addition to a slight normal displacement. This conception is in accordance with the idea advanced by Jeffries of $(111)\gamma$ to $(110)\alpha$ transformation with accompanying multiplicity of ferrite orientations. Investigation conducted by Mehl, Barrett, and Smith (24) not only has served to confirm the results of Kurdjumow and Sachs, but also to show that this crystallographic translation occurs on the γ-α reaction in pure iron and on the formation of ferrite in slowly-cooled hypo-eutectoid steels.

The location of carbon in martensite is a problem concerning which experimental evidence is not available. The question may be considered on the basis of lattice structure and density calculations. The solid solution, austenite, is believed to be of the interstitial rather than the substitutional type. On the assumption that the carbon in martensite is also interstitial, the carbon atom may be located at the base of the tetragonal lattice. In general it is believed that the carbon in austenite and martensite should be considered as the carbon atom and not the Fe_3C molecule.

Various investigators have considered the possibility of more than one kind of martensite. Emmons (25), in his studies of high speed tool steels, refers to the martensite formed on quenching as 'primary' martensite. The decomposition of retained austenite on tempering produces a 'secondary' marten-

site--possessing physical properties similar to the primary product. Hanneman and Schrader (26) have suggested the possibility of a peritectoid martensitic system, consisting of two metastable phases in metastable equilibrium with austenite. The epsilon phase has nearly the same structure as ∝ferrite, but has the ability to dissolve considerably more carbon. On tempering, epsilon decomposes to produce ∝ferrite with accompanying carbon precipitation.

In general, it may be stated that there are at least two forms of martensite. Freshly quenched martensite consisting of a body-centered tetragonal lattice is termed ∝martensite. Tempering causes a change toward a body-centered cubic system and produces ∝ martensite. In low carbon steels, the raising of the Ar″ temperature causes tempering of the martensite to occur soon after its formation, so that the tetragonal structure may not exist for a measurable time interval.

Martensitic Hardness

The most interesting property that martensite possesses is extreme hardness, and it is not surprising that many explanations have been offered for this phenomenon. One of the first ideas advanced was that of extremely fine grain size. Jeffries and Archer (27) indicated that the individual martensite grain possessed a diameter of 100 to 200 atom diameters. Heindlhofer and Bain (28), however, as the result of x-ray diffraction studies combined with the use of the petographic mi-

croscope concluded that martensite consists of distorted ferrite units of approximately the same grain size as the original parent austenite grain. Westgren (29) has called attention to the fact that the possibility exists that x-ray patterns may cause martensite to appear coarse grained, whereas it is actually composed of a mass of very small crystals oriented nearly parallel. The actual grain size of martensite is still a disputed point. The tetragonal structure of martensite itself is not considered to be of importance as far as hardness is concerned, because the process of tempering--i.e., change to a cubic structure-- is accomplished without marked decrease in hardness.

The discovery of the phenomenon of age hardening suggested to Rosenhain (30) an analogy between this process and quench hardening. Martensite, as has been shown previously, consists od a highly supersaturated solution. A structural alteration during quenching (not necessarily resulting in actual precipitation) may account for the hardness.

The presence of lattice distortion, as shown by x-ray studies, has been considered the main factor in causing hardness of martensite. Fink and Van Horn (31), however, observed marked softening of brass samples whose lattice structures were very definitely distorted. Bain and Heindlhofer (28) concluded that, although there is an appreciable amount of lattice distortion due to twisting of ferrite planes, the primary reason

for excessive hardness is more probably the strong interatomic bonding present in the supersaturated solid solution. Interstitial position of carbon atoms producing distortion of ferrite lattice would also possess ability to form strong interatomic bonds characteristic of Fe_3C.

Experimental Method

After consideration of the various experimental procedures, it was decided to attempt to develop a technique for simultaneously measuring volume and magnetic changes. Lack of time necessary for constructing an apparatus capable of such measurements below the Ar″ temperature, however, necessitated a change in the mode of attack. Sufficient work was completed to indicate an apparatus which may serve as a means of obtaining such data. Further investigations along this line will be carried on.

The method that was finally adopted to obtain data for this research consists of a metallographic procedure similar to that used by Greninger and Troiano (16). The method is based on the fact that proper etching of metallographic samples will distinguish clearly between tempered martensite and quenched martensite. This difference in etching characteristics between tetragonal and cubic martensite has been demonstrated previously by Hanneman (32).

In brief, the process consists of quenching samples from the austenitic field to a given isotherm below the Ar″ temperature for a measured time interval; then tempering at a temperature above the Ar″ ; and finally quenching to room temperature. The martensite formed during the first quench, together with that formed at the isotherm, appears as a dark acicular structure against a white background. The white matrix consists of

martensite (and probably some retained austenite) produced during the final quench, but represents the undecomposed austenite at the end of the isothermal treatment.

The first difficulty in conducting isothermal transformations is achieving extremely rapid quenching rates. The ideal condition would be to reach the temperature of the isotherm instantaneously. Such a condition, of course, can only be approached by proper consideration of the specimen size and quenching medium. At any rate, it is necessary to reach the lower temperature before any isothermal decomposition can commence -- assuming the reaction does occur according to the S-curve theory. The short lag times reported in S-curve work in the lower regions necessitates very rapid cooling rates. If the martensite formation occurs during the cooling process itself, then quenching need only produce cooling faster than the critical cooling rate. It is necessary to use cooling rates greater than the critical in order to prevent Ar′ transformation. Cooling rates faster than the critical should have no effect on the rate of martensite formation according to the theory of Carpenter and Robertson. However, since it is undesirable to arbitrarily rule out the possibility of S-curve transformation, as rapid cooling rates as possible are required for the investigation.

In studies of decomposition rates of austenite, there is a means available to retard the reaction to any chosen rate,--

namely, the addition of various alloying elements as shown by Bain (33). Although the mechanism of martensite formation in alloy steels may be exactly similar to the formation in plain carbon steels, it is desirable to study the problem first in its simplest form. After the nature of the martensite formation in plain carbon steels is settled, application to the vast field of alloys should be made. The argument may be advanced that unless specially prepared iron-carbon samples are used, the study is actually concerned with alloy steels because of the various elements present in commercial steels. Nevertheless, this investigation is confined to the study of the class of commercial steels usually designated as plain-carbon. The samples used in this work contained 0.80% carbon and 0.64% manganese.

In order to obtain rapid cooling, thin sections were used for samples. The specimens were cross sections cut from rods 0.18 inches in diameter and rough polished to a thickness of 0.045 inches. The quenching and tempering baths consisted of six pounds of a quarternary eutectic of 27.3% lead, 49.5% bismuth, 10.1% cadmium, and 13.1% tin--possessing a melting point of 70°C. The two metal baths were maintained at a constant temperature by means of proper controllers. Temperatures in the molten metal and in the heating furnace were measured by means of a potentiometer and alumel-chromel thermocouples calibrated against pure lead and antimony. The quenching and tem-

pering bath temperatures were controlled within 2°C.

For the preliminary heat treating process, the specimens were soaked at 750°C for one hour, followed by a furnace cool. In order to prevent excessive scale formation or decarburization during the treatment, a nitrogen atmosphere was maintained. Numerous investigations have shown the necessity for removing the last traces of water and oxygen in order to avoid any surface loss of carbon. However, for the purposes of this work, it was found that sufficient purification was obtained by passing the tank nitrogen over steel wool at 1000°C before sending the gas into the heating furnace. The very slight oxide skin formed on the surface of the sample apparently acted as a protective coating in retarding decarburization. Figure 4 illustrates the amount of decarburization that occurred during the preliminary heat treatment. It is evident that the sample is very close to the eutectoid composition.

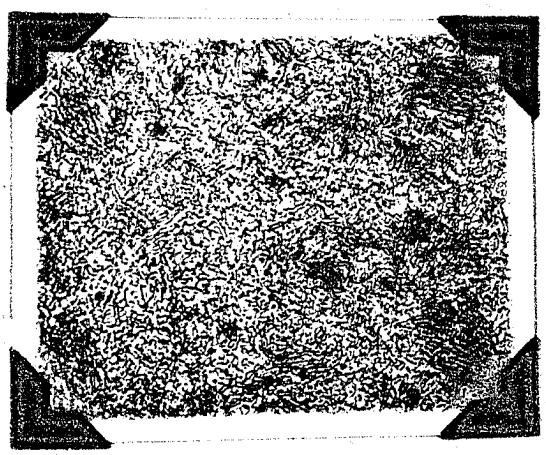


Figure 3

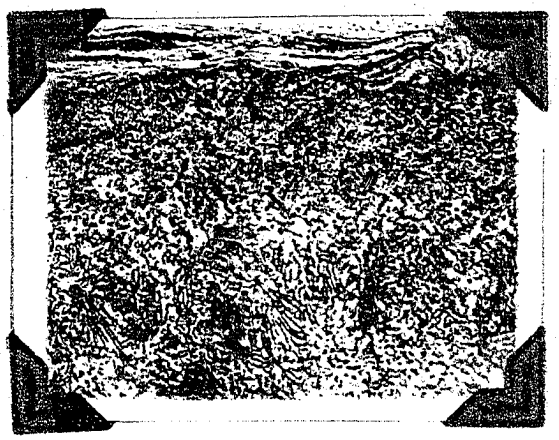


Figure 4

The prepared samples were suspended from a 16 gauge iron wire in the heating furnace for thirty minutes at 750°C-775°C. In the beginning, a small hole (#60 drill) was drilled through the specimen. A 27 gauge steel wire was threaded through this hole to suspend the specimen from the iron wire. Unfortunately, the presence of the hole added considerably to the difficulty of polishing the samples. It was found, however, that the samples could be held satisfactorily by merely winding the steel wire around the lateral surface of the piece,--the wire being supported by means of small notches filed in the lateral surface. This procedure was followed in samples 25 to 35.

The metallographic method has been shown by Davenport (34) to be the most sensitive to variations in the composition of the austenite. Diggs (35) has conducted a study on the effect of non-uniformity of austenite on the rate of austenite decomposition. Transformation proceeds with greater rapidity in low carbon areas, making it difficult to evaluate the average per cent decomposition in any given sample. Accordingly, it is necessary to use a soaking time that will insure complete solution of the carbides, and homogenization of the austenite. Lauderdale and Harder (36) have determined the time necessary for carbon to go into solution in order to develop full hardness on a quench. Using 0.77%-0.78% carbon steels, it was found that from one to two seconds is sufficient at 870°C, and from five to seven seconds at 815°C. With these soaking

times, however, there is incomplete solution of the carbides. A spherodized structure resulted in complete solution at 870°C in one minute, but in some cases the last of coarse carbides had not dissolved in one hour. These results indicate that the chosen soaking time of thirty minutes was sufficient for the samples used. In some cases, the specimens were heated to a much higher temperature, and for a longer time interval. Examination of these samples failed to reveal any differences from those run at a lower soaking temperature and quenched for the same time interval.

The transfer of the samples from one unit to another was accomplished in approximately one second. After being immersed in the quenching bath for a pre-determined time interval, the specimens were tempered for five seconds at 278°C. The final quench to room temperature was accomplished in 500 cc of a 10% NaOH solution.

In order to facilitate the handling of the samples during polishing, they were mounted in a low carbon steel holder. The samples were set into small holes drilled in the surface of the steel. In this way, several specimens could be mounted in one holder, thus decreasing the amount of polishing required. It was found that the most convenient size for polishing was a 3/4 inch diameter section holding four samples. However, in some few cases, as many as eight specimens were mounted in a single holder.

Mounting mediums such as lucite or bakelite are prohibited because of the injurious effect of re-heating the samples. It is necessary to exercise considerable care in the polishing technique in order to minimize surface heating. A dry polishing procedure was adopted for preliminary preparation of samples down to the 000 paper. Wet wheel polishing on felt wheels, first with 600 alumina, and finally with levigated alumina, completed the polishing operation. A two per cent solution of nitric acid in absolute alcohol was used as an etchant. In order to prevent the formation of an oxide film after etching, the specimens were washed thoroughly in running water, then given two successive alcohol rinses, and finally were dried by compressed air. It was found that the microstructure was appreciably improved by re-polishing with the levigated alumina , and etching a second time.

Figures 5 to 24 illustrate the microstructure of a series of specimens that represent the transformation at two separate isotherms,-- 210°C and 155°C.

Transformation at 155°C

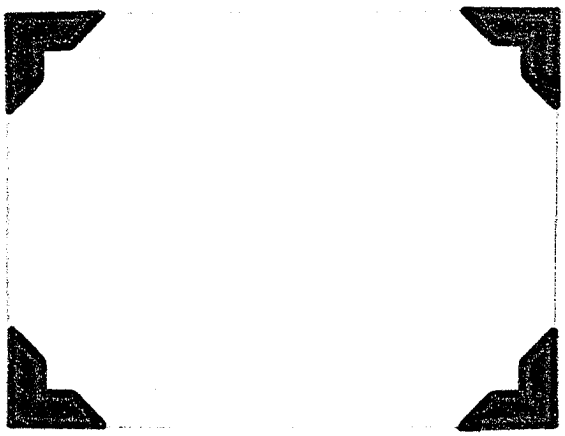


Figure 5. ~ <1"

Figure 6 ~ 1"

Figure 7 - 2"

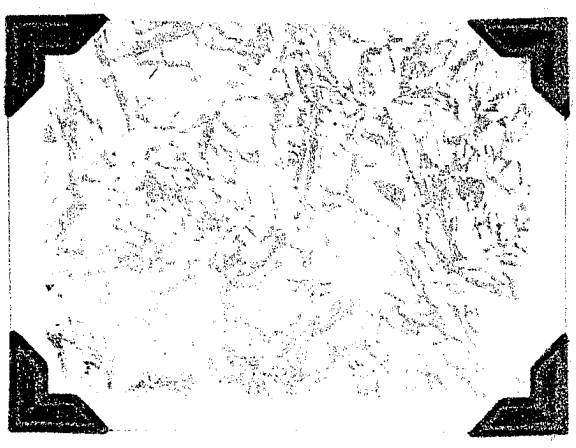


Figure 8 - 30"

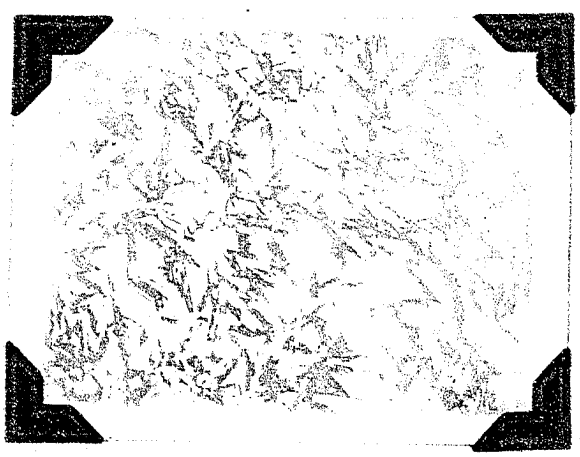


Figure 9 - 60"

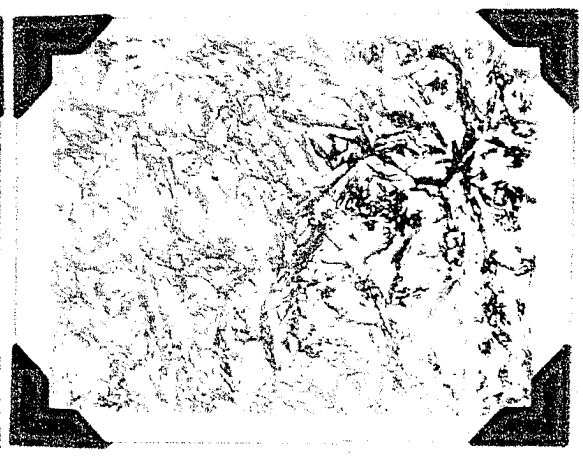


Figure 10 - 2'

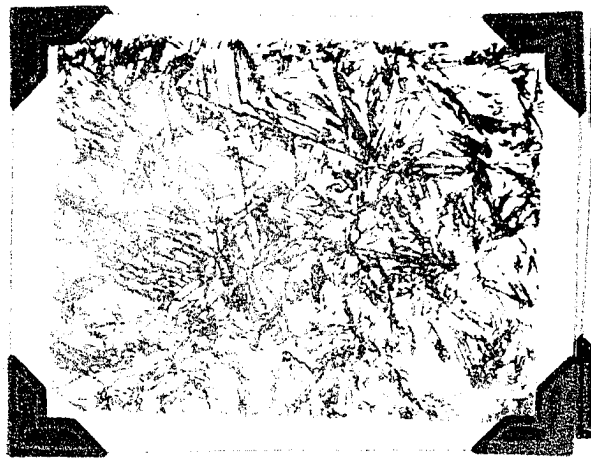


Figure 11 - 20'

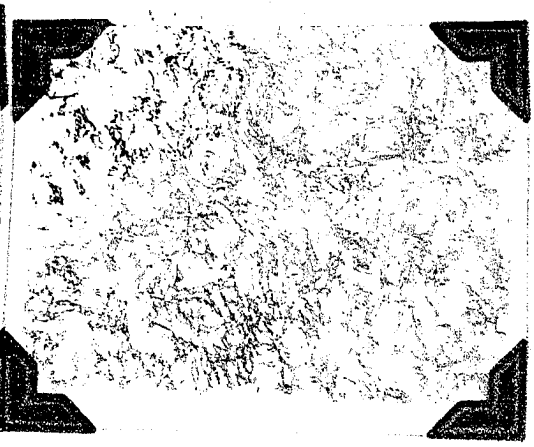


Figure 12 - 30'

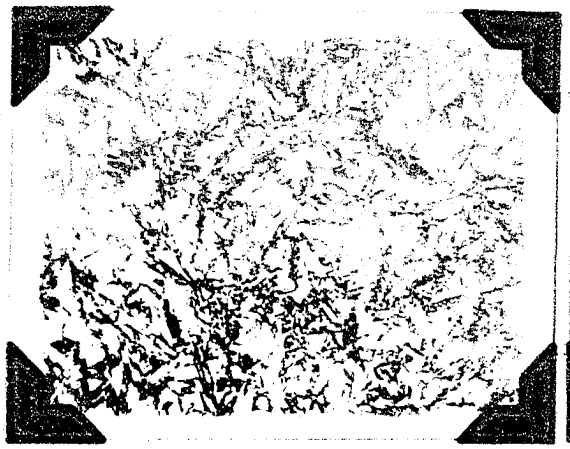


Figure 13 - 60'

Figure 14 - 12 hrs.

Transformation at 210°C

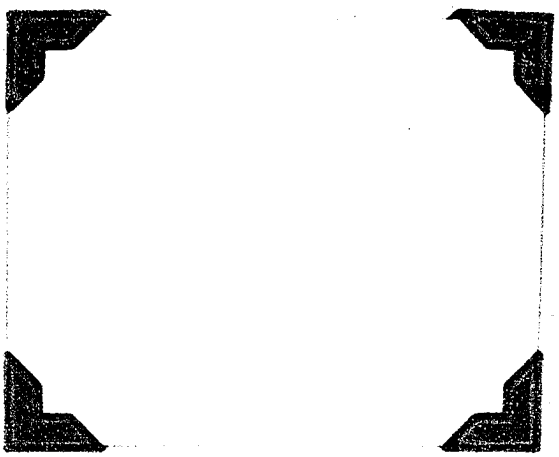


Figure 15 - <1"

Figure 16 - 1"

Figure 17 — 2"

Figure 18 — 5"

Figure 19 — 10"

Figure 20 — 30"

Figure 21 - 60"

Figure 22 - 10'

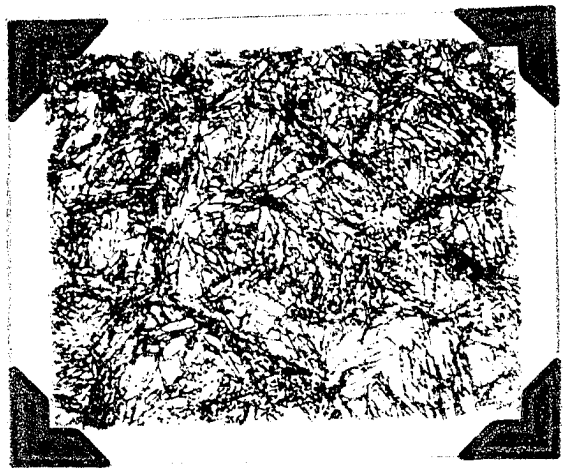


Figure 23 - 30'

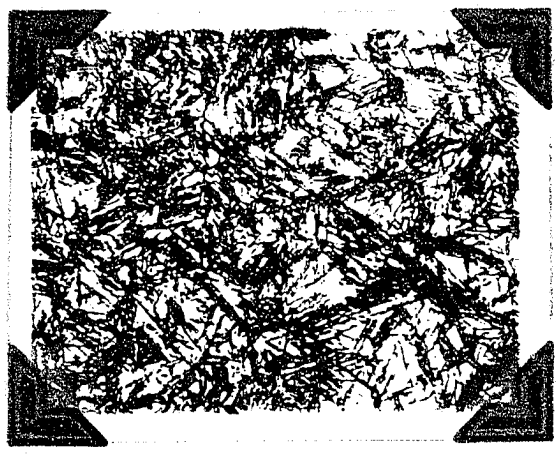


Figure 24 - 1 Hr.

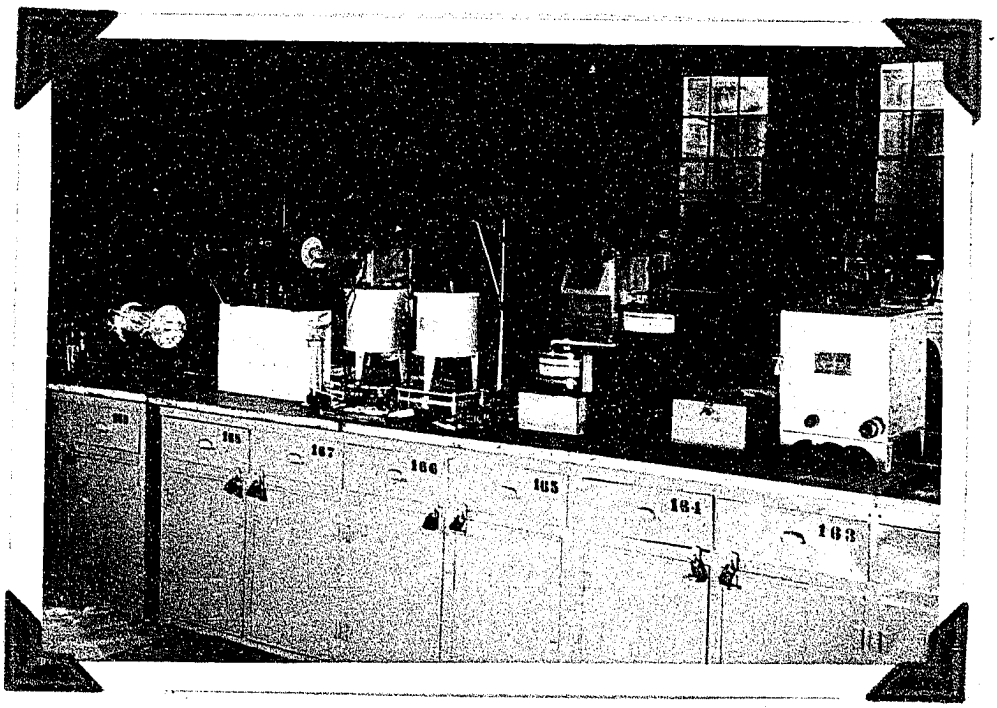
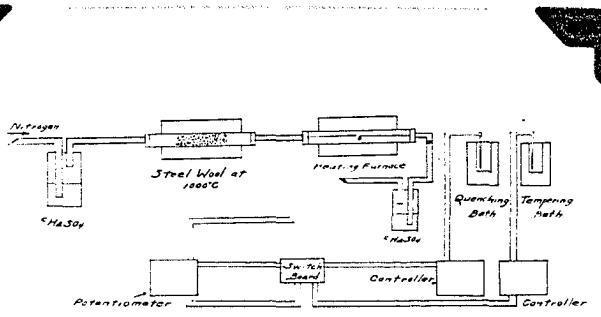


Figure 25 - Apparatus



Sketch of Apparatus

Figure 26

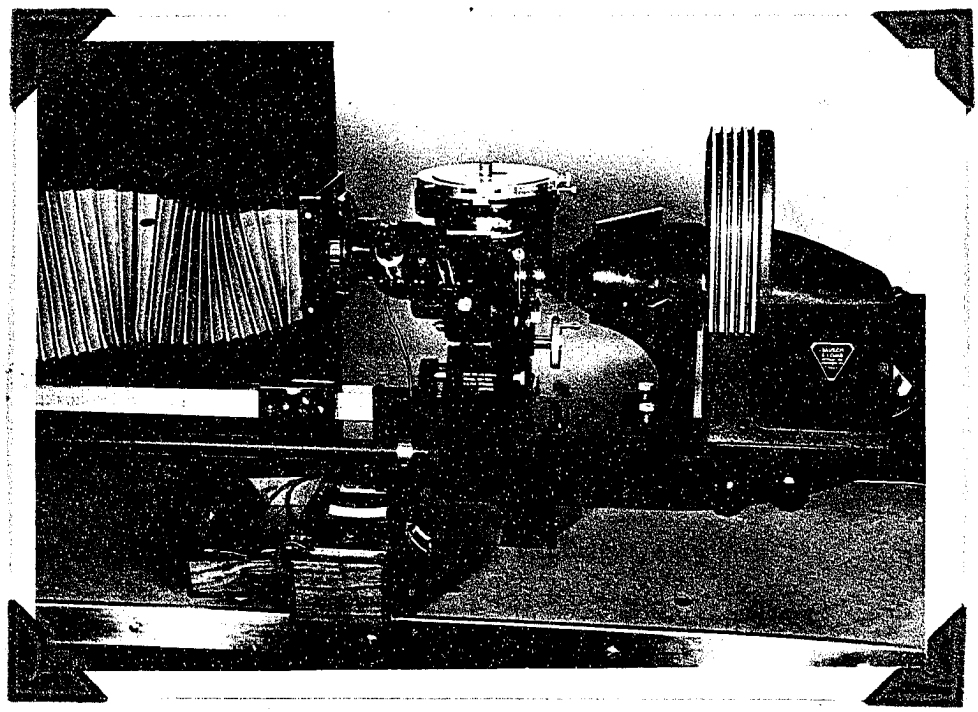


Figure 27

Metalloscope with Photometer in Place

Method for Evaluation of Results

The metallographic method for following transformations is often avoided because of its tediousness. In the first place, the large number of samples that must be handled and the necessity of polishing each sample is time consuming. Secondly, even after the samples have been properly prepared, the actual evaluation of the transformation has proven to be a laborious and inaccurate process. Previous methods have been concerned with the evaluation of the per cent of a photomicrograph covered by the dark martensite needles. Counting the number of squares on a super-imposed cross-sectional paper which is necessary to cover the dark areas is one method often used. Cutting out and weighing the tin foil necessary to cover the dark needles is another procedure available. The line intercept method has also been of value in analyzing results. It is obvious upon referring to Figures 5 to 24 that each of these methods offers numerous difficulties. At high magnifications, a photomicrograph represents but a very small fraction of the area of the specimen. A slight variation in the martensite formation may easily cause a large error in the computation of the per cent present. At lower magnifications, however, it becomes increasingly difficult to apply any of these methods because of the small size of the martensite needles.

A more rapid and accurate method has been developed to de-

termine the per cent martensite present. The sample is placed upon the stage of the metallöscope, and the amount of light reflected from the surface is then measured with a photometer. The photometer cell is located at the bellows entrance in place of an ocular. A specimen which shows zero transformation (i.e. no dark needles) will give the maximum reading, whereas a sample transformed completely results in a minimum amount of feflected light. For the 0% transformed, an average value of 4.50 foot-candles for the samples showing no needles was used. For the lower limit, a sample was quenched from 775°C to room temperature in 10% NaOH, tempered for thirty seconds at 278°C, and re-quenched in the caustic. The resulting microstructure gave a photometric reading of 0.65, thereby providing a range of 3.85 foot-candles.

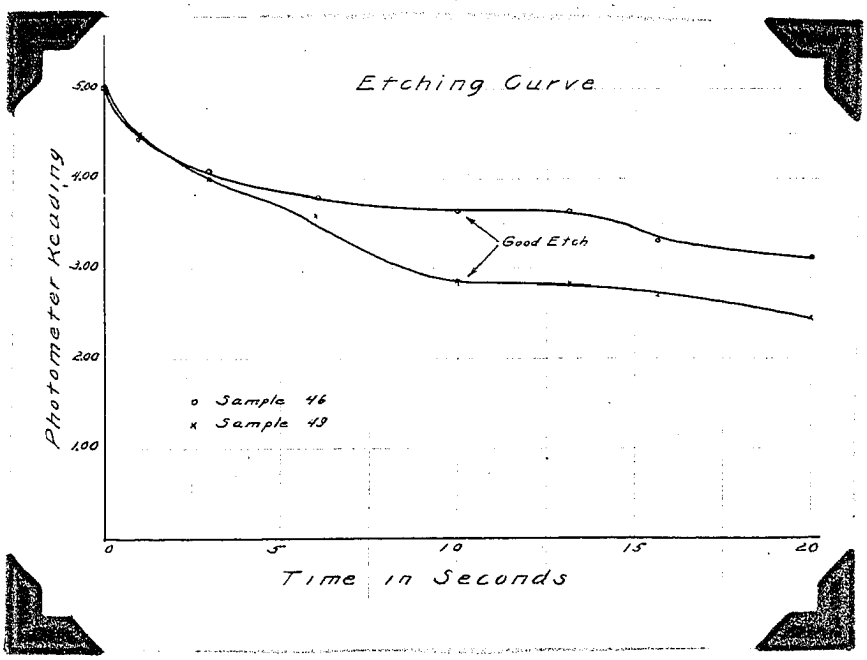


Figure 2.8.

Samples which have transformation between these two limits give corresponding photometer readings which can be used directly to interpolate for the amount of martensite present. A straight line relationship was found to exist between the photometer reading and the total amount of light incident on the surface of the cell. Figure 29 represents data obtained upon covering various sections of the cell surface with white paper as a mask.

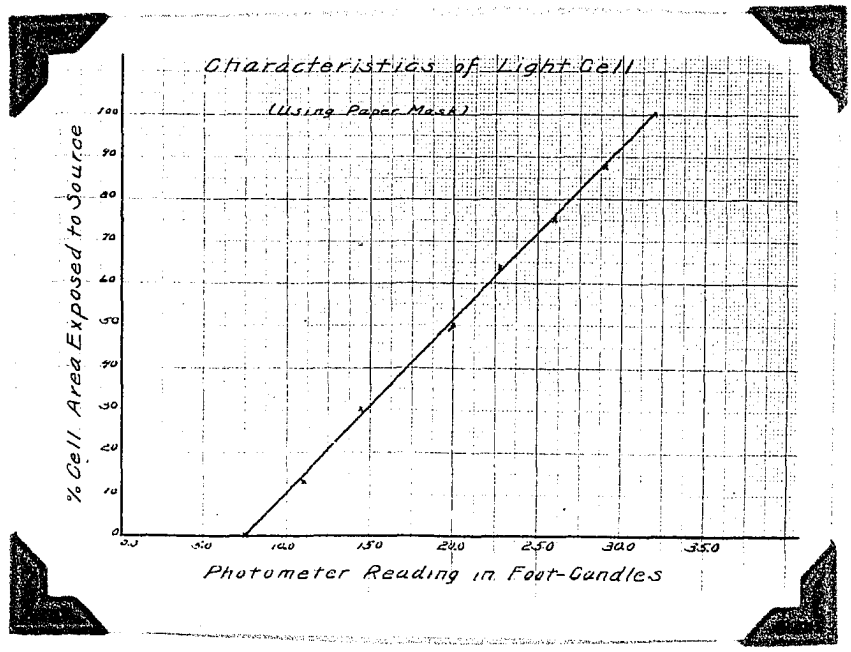


Figure 29

A method such as this, first of all, requires a constant source of illumination. A mercury vapor tungsten filament bulb served to provide a source of light which decreased very slowly with continued use. The illumination was adjusted by

means of a diaphragm to a value of 5.00 foot-candles when a brightly polished surface was placed on the stage of the microscope. In this way, the intensity was checked before and after the examination of each specimen.

In order to compare the extent of transformation in various samples by a photometric method, it is necessary that the specimens be etched to the same degree. If the nature of the transformation product below the Ar″ line is the same regardless of the time or temperature used, it follows that the time required for etching the various samples should be a constant. However, any variations in the temperature and nature of the specimen surface would influence the rate of attack by the etchant. In addition, it is necessary that the etchant used be constant in composition. The influence of these factors can be minimized by proper etching technique. Handling the specimen with tongs to prevent temperature changes, rinsing the surface in xylol prior to etching to remove any oil film, and frequent changing of the etchant are precautions to be observed.

Despite extreme care in the etching process, it was found that the more highly transformed samples required a longer etching time to develop the structure. Etching curves (photometer readings vs. time of etch) were determined for a variety of specimens. In all cases, a characteristic plateau, corresponding to an etch which appeared satisfactory upon visual examination, was obtained. The data for the first curves was ob-

tained by superimposing successive etches upon the specimen. Such a procedure is subject to criticism because of the increased effect of oxide film on the sample,-- leading to pronounced spotting after five repeated etches. Reliable data, however, can be obtained by repolishing the specimen after each etch. The representative curves, illustrated in Figures 28 and 30, were obtained by the latter method.

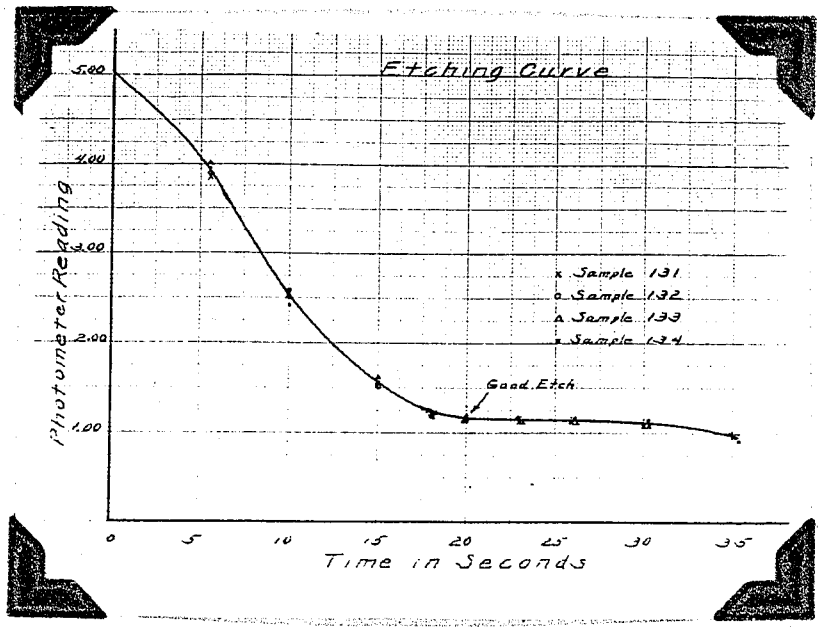


Figure 30

In order to facilitate the examination of the same field each time, the samples were marked by a microcharacter with two intersecting lines,-- the intersection being located in the center of the field of view for each examination. The presence of these scratches caused the photometer reading to be lowered by about 0.03 foot-candles, and therefore may be considered to have a negligible effect.

The fact that the plateau occurs at different times, as shown by the figures, adds to the difficulty of evaluation. Using the same etching time for the more highly transformed samples develops the structure, but produces brown colored needles. Further etching darkens the needles, and a plateau is reached. It is not possible to choose any one etching time to use for all samples. For quantitative results, it is necessary to determine an etching curve for each sample and to use the value of the photometer reading at the plateau as representative of the transformation. The quantitative nature of the method is evidenced by the agreement within 2% of the values obtained on etching curves determined by two separate observers. Greater accuracy of measurement is unnecessary because of the obvious errors inherent in the method itself. Indeed, it seems highly probable that variations of a few per cent are met with in the cross sections reached by the repeated polishing procedure. Extreme care must be exercised in the polishing and the etching of each specimen.

Since, in all cases, the plateau begins at an etching time corresponding to a good etch by the visual standard, and ends when darkening of the matrix indicates that over-etching has occurred, it is possible to evaluate the samples more rapidly but less accurately. Without determining an etching curve for each sample, the specimens are merely etched for the length of time that is necessary to produce a sharply defined structure. This procedure has been adopted for most of the data tabulated, in order to indicate qualitatively the rate of reaction. In all cases, the 21x objective was used because it focussed a pencil of light slightly smaller in cross section than the sample itself. The photometer reading, of course, represents an integrated value over the entire field of view.

Data

Data

Sample Number	Temperature °C	Time	Photometer Reading	% Martensite
19	247	1"	4.40	0
20	247	2"	4.45	0
21	248	5"	4.40	0
22	249	10"	4.44	0
24	248	10"	4.47	0
25	248	1'	4.42	0
26	249	2'	4.44	0
27	248	5'	4.37	3
28	248	5'	4.32	3
29	249	10'	3.95	14
30	249	15'	3.35	30
32	249	20'	2.10	67
34	248	7'	4.20	8
35	247	13'	3.90	16
36	247	17'	2.15	61
37	247	30'	1.35	81
38	247	1 hr.	0.90	92
94	240	1"	4.48	0
95	240	3"	4.40	2
96	239	10"	4.40	2
97	239	18"	4.40	2
98	239	1'	4.39	2

Sample Number	Temperature °C	Time	Photometer Reading	% Martensite
99	240	5'	4.38	3
100	240	10'	4.35	4
101	240	30'	2.45	53
102	240	1 hr.	1.25	82
103	240	6 hrs.	1.10	88
4	225	<1"	4.43	0
8	224	>1"	4.36	4
9	225	5"	3.82	17
12	225	60"	3.85	16
13	224	2'	3.80	18
15	224	5"	3.78	18
16	225	5'	3.76	19
17	225	10'	2.80	44
18	225	20'	1.30	83
41	210	<1"	4.38	3
39	210	>1"	3.90	16
40	210	2"	3.75	19
42	210	5"	3.68	21
43	210	10"	3.64	22
44	209	15"	3.50	26
45	209	30"	3.60	23
46	209	60"	3.60	23
88	208	5'	3.00	39
89	208	10'	2.70	47

Sample Number	Temperature °C	Time	Photometer Reading	% Martensite
90	208	30'	1.50	78
91	208	60'	1.45	79
92	208	120'	1.30	83
75	179	1"	4.45	0
76	179	2"	4.43	2
77	179	10"	2.50	52
78	179	60"	2.47	52
80	181	10'	2.40	55
81	179	15'	2.35	56
83	179	30'	2.20	50
84	179	45'	2.00	65
85	181	60'	1.85	69
86	180	90'	1.70	73
47	155	<1"	4.50	0
48	155	1"	3.85	16
49	155	2"	2.75	45
50	155	5"	1.68	73
51	155	10"	1.62	74
52	154	20"	1.60	75
54	155	30"	1.58	76
55	155	45"	1.60	75
56	155	60"	1.52	77
57	155	2'	1.55	76
58	155	6'	1.50	78

Sample Number	Temperature °C	Time	Photometer Reading	% Martensite
59	155	10′	1.40	81
60	154	20′	1.38	82
61	154	30′	1.40	81
62	156	45′	1.50	78
63	156	60′	1.50	78
64	155	12 hrs.	1.20	86
65	137	1″	2.80	44
66	137	2″	1.55	76
67	137	10″	1.30	83
68	138	60″	1.27	84
70	137	7′	1.24	85
71	138	15′	1.25	85
69	137	30′	1.29	83
72	138	60′	1.23	85
73	138	5-1/2hrs.	1.26	85
125	122	2″	1.95	69
126	122	5″	1.15	87
128	122	60″	1.09	88
129	122	5′	1.10	88
130	122	10′	1.15	87
131	122	30′	1.10	88
132	122	60′	1.14	87
133	122	2 hrs.	1.12	88
134	122	4 hrs	1.10	88

Sample Number	Temperature °C	Time	Photometer Reading	% Martensite
135	122	44-1/2hrs.	1.10	88
111	98	2"	1.75	71
112	98	10"	1.00	91
113	98	60"	1.03	90
116	98	5'	1.05	90
114	98	12'	1.07	89
115	98	45'	1.02	90
117	99	95'	1.03	90
118	99	2-1/2hrs.	1.08	89
119	99	8 hrs.	1.10	88
104	91	1"	1.60	75
105	90	2"	0.96	92
106	90	20 "	0.97	92
108	90	60 "	0.95	92
109	91	5'	0.92	93
110	91	15'	1.00	91
120	91	37'	0.95	92
121	91	60'	0.96	92
122	91	2 hrs.	0.98	91
123	91	4 hrs.	0.99	91
124	91	20 hrs.	1.00	91
136	25	——	0.65	100

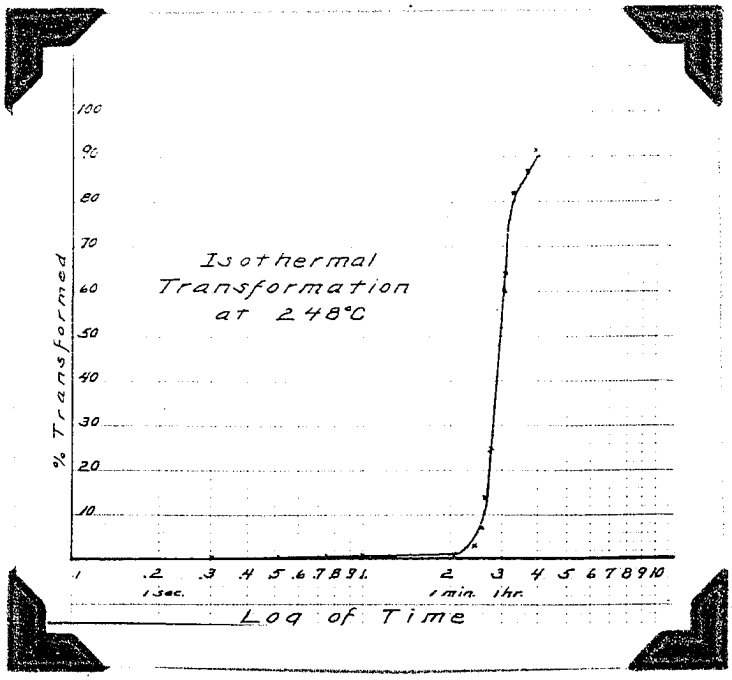


Figure 32

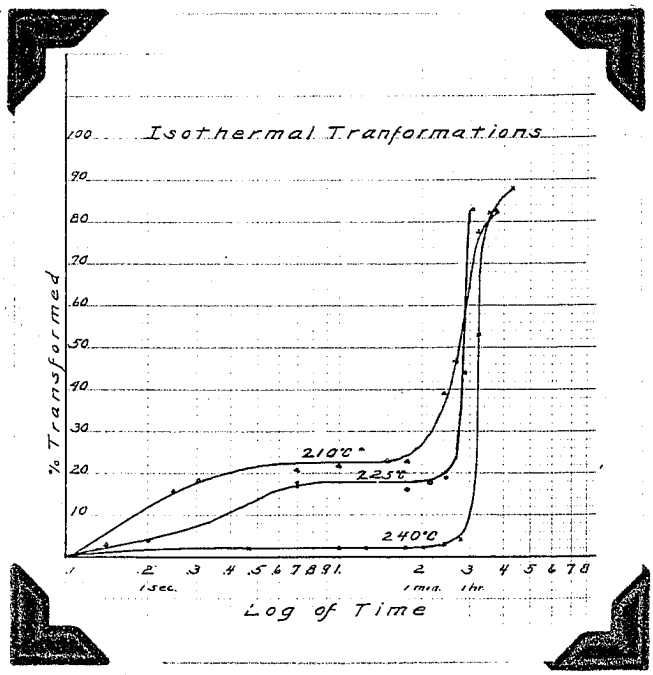


Figure 31

Discussion of Results

Figures 31 to 35 summarize the results obtained in this investigation of martensite formation in plain-carbon steels. Transformation at 248°C appeared to take place according to an S-curve reaction. At this temperature, there is a lag time of about six minutes prior to any austenitic decomposition. Transformation then commences and proceeds steadily toward completion. Additional data are necessary to determine the exact nature of the transformation curve as the reaction approaches completion. In all probability , the curve would approach the 100% transformed line asymptotically. The lag time is in good agreement with that reported previously by Bain and Davenport (5). The microstructure of the isothermal product at 248°C is shown by Figure 37. Although quite similar to the martensite needles shown in Figures 5 to 24, there are a few differences apparent. The product of higher temperature transformation tends to come out in longer, more slender needles. These needles form in groups or clusters indicating that the reaction may be dependent upon a diffusion process. The product of transformation in this range is usually designated 'bainite'.

The sample run at 240°C for only three seconds showed a small percentage of needles present. From three seconds to ten minutes, the amount of transformation remained nearly constant . At the end of this time interval, steady transforma-

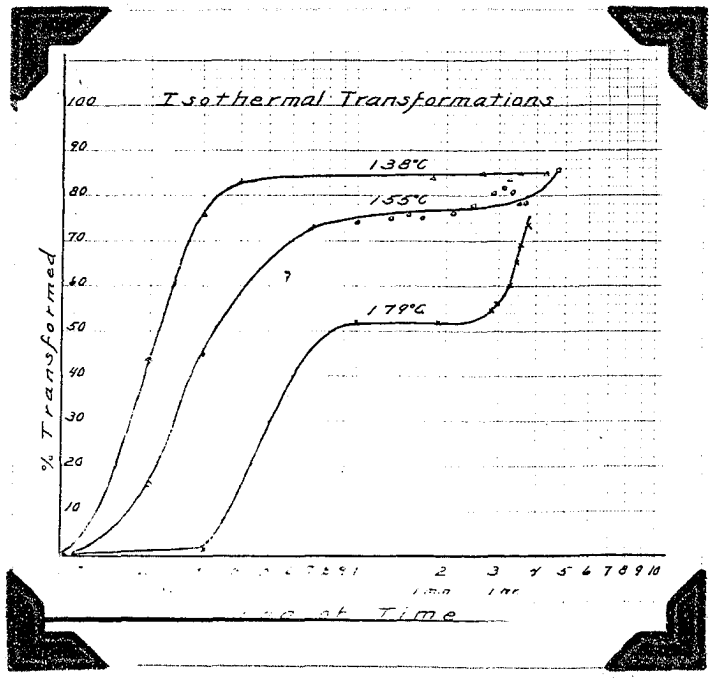


Figure 33

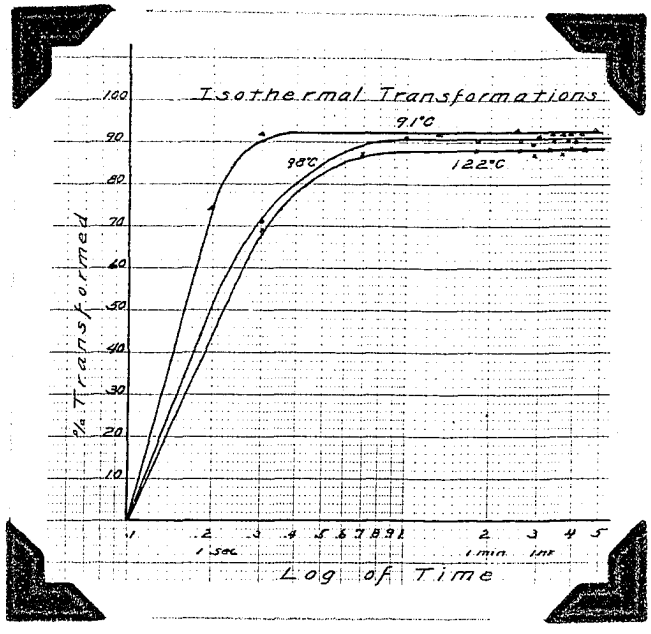


Figure 34

tion toward completion commenced (Figure 31). A similar mechanism of reaction was found at all isotherms investigated below 240°C. The lower the temperature, the greater the amount of transformation produced when the plateau in the curve was reached. (Figures 31,33,34). At the isotherms below 155°C, insufficient data were obtained to determine the transformation after the plateau is passed. The time interval before the plateau of the reaction is reached may indicate that a rapid primary reaction has occurred, or that the size of the sample prevented quenching to the isotherm within this time. It seems more reasonable that the latter is true, and that the data obtained for transformation times less than two seconds should be disregarded. If this is done, in all cases below 248°C there appears to be a definite amount of an initial product which forms during the cooling operation. Upon maintaining a sample at a given isotherm, further transformation begins after a certain time interval. The amount of the initial product formed is solely a function of the temperature drop between some limiting temperature and the isotherm,--the greater this difference, the greater will be the amount of transformation. Figure 35 illustrates the formation of this quenching product as a function of the temperature drop. This curve was obtained by plotting the values of the per cent transformed at the plateau of each isotherm. The data for the lower tempera-

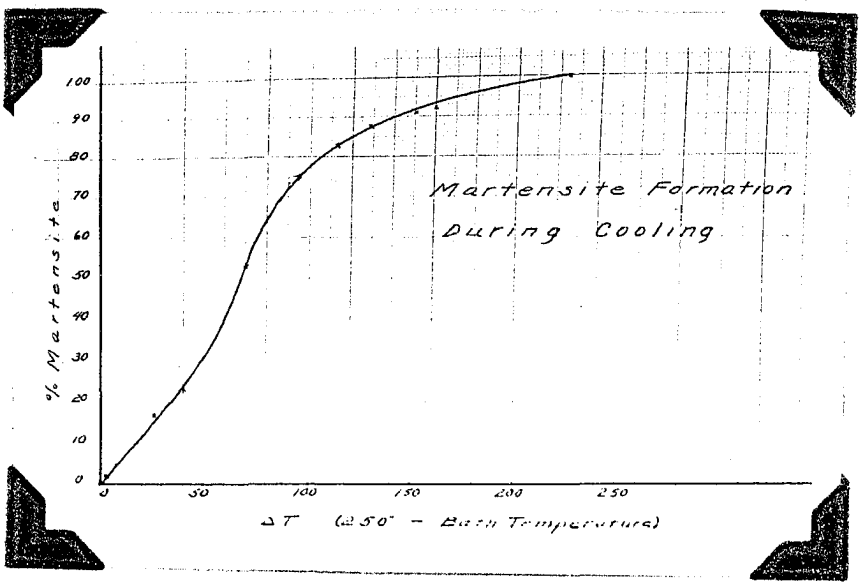


Figure 35

tures are probably less accurate because of the difficulties in differentiating between highly transformed specimens.

The austenitic decomposition product formed during cooling in the low temperature region should be designated 'martensite'. The difference in the reaction at 248°C (no product upon cooling to the isotherm) and 240°C (slight transformation during the quenching process) indicates that the Ar" temperature lies somewhere between these two isotherms. This temperature which bounds the martensite region is apparently independent of cooling rates. The Ar" value found is in good agreement with previous results reported for a 0.80% plain carbon steel.

The product resulting from transformation at the isotherm, although microscopically similar to martensite, should be classified as a member of the bainite family. As has been noted previously, not enough data were obtained to establish the mechanism of the bainite formation. However, the lower the temperature, the slower the bainite reaction occurred. At 122°C, no isothermal product was apparent after 44-1/2 hours had elapsed.

In many of the samples studied, it was found that a heavy needle formation took place around the edge prior to any transformation throughout the specimen. Figure 36 illustrates this 'edge effect' in a specimen that was abnormal in this respect. Robertson (9) has mentioned a similar formation in his samples,

Figure 36

Figure 37

and reasoned that it was probably due to a pressure effect. If this is true, there is no apparent way of avoiding such a formation. Another explanation is based on the more rapid cooling rates at the edges. If this were the only cause, it follows that in the samples quenched for more than five seconds, the edge effect would be missing. The entire sample should reach the isotherm in two or three seconds and therefore show a constant amount of martensite across the surface since the entire piece has passed through the same temperature range. In general, the edge effect was less pronounced for these longer time intervals, but was still apparent. A third explanation could be based on the lowering of the carbon content at the edges during the heating and soaking period. The decarburization would cause the raising of the Ar'' temperature near the edges, and consequently give a greater amount of martensite in these regions upon quenching to an isotherm. The negligible amount of decarburization during the heat treating process indicates that this last explanation is not satisfactory, although it may have some small effect.

The reason for the difference in etching time for the various samples is not readily apparent. However, if the process of etching is considered from the electrolytic viewpoint with the needles as anode and the matrix as cathode, it seems logical that a greater etching time would be necessary the greater the amount of anode area present. This is in general agree-

ment with the results obtained. In order to clearly establish this relationship, rigid control of the variables in the etching technique must be made.

In conclusion, it should be emphasized that the results reported have been obtained in a qualitative manner only, and should be interpreted on that basis. Although a large number of samples was prepared and examined, not enough data were obtained to conclusively establish the nature of martensite formation. It is quite possible that the reaction curve of Figure 35 actually will show a decrease in the martensite formation below 91°C due to the presence of retained austenite. Further data are needed to determine the curve characteristics at the lower temperatures. In general, however, it may be said that this investigation substantiates the theory of Carpenter and Robertson, and confirms the work of Greninger and Troiano.

Summary

The results of this research indicate that transformation of austenite at temperatures below the Ar" occurs in two separate stages. Martensite formation takes place during the actual cooling process, and is a function of the temperature interval between the Ar" and the chosen isotherm. Further transformation of the austenite at this isotherm takes place after a definite time lag - producing a bainite structure. Consequently, the Carpenter-Robertson theory of martensite formation has beeb substantiated, and the S-curve theory disproved.

A photometric procedure for the evaluation of the amount of decomposition product present in the microstructure of the various samples has been developed. The method, in brief, consists of measuring the amount of light reflected from the surface of the properly etched sample.

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