# A Personal Commentary on "Transformation of Austenite at Constant Subcritical Temperatures"\*

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THE first recorded citation of the word "bainite" is in an article<sup>[1]</sup> published 12 years after Davenport and Bain introduced isothermal transformation as a technique to study the progressive evolution of phases as a function of time and temperature. This long interval is a reflection of the fact that although the phase was named in 1934, it was not used even by Bain and his coworkers in articles published subsequently, referring instead to a dark etching acicular aggregate somewhat similar to martensite.

Anyone who reads the 1930 article, I think, would agree with me that such modesty, although laudable, was not needed given the breathtaking quality of the experimental work and the number of insights revealed, some of which have now become legend.

The sheer amount and depth of experimental work reported in the article is impressive. Take, for example, the dilatometry. In order to avoid complications resulting from the expansion of the dilatometer rods themselves, a substantial part of the equipment was immersed into the molten lead bath to achieve the desired temperature. The specimen grips were designed to be self-aligning because the hot sample in its austenitic condition had to be introduced quickly before the assembly again was immersed into the molten metal.

The dilatometric measurements were sufficiently accurate to note that during the formation of bainite or martensite, "the volume change is not necessarily uniformly reflected in all dimensions. Indeed, the thickness of flat disk specimens actually decreases as the volume increases." The observation was not explained at the time, but we now know that this is a consequence of anisotropic transformation plasticity resulting from crystallographic variant selection. Indeed, the exploitation of such anisotropy is the basis of methods for designing welding alloys capable of compensating for the thermal contraction that leads to pernicious residual stresses. [2]

Davenport and Bain achieved their goal of introduc-

ing a "time factor to the iron-carbon [equilibrium]

particularly revealing (Figures 11 and 12). Transformation rates in these alloys are retarded sufficiently to avoid overlap between different reactions. They provide the first clues that the diagram really consists of two sets of C curves, one for ferrite or pearlite, which form at high temperatures, followed by a gap until a temperature is reached in which bainite forms. This is a consequence of changes in atomic mobility leading to different transformation mechanisms as the temperature is reduced. Zener in 1946<sup>[3]</sup> recognized this in his classical theoretical article on the kinetics of transformations in steels in which his idealized TTT diagram consisted of two sets of separated C-curves in the manner described. This two-curve representation forms the basis of a vast number of quantitative treatments of steels and emphasizes the distinction between transformation mechanisms.

The second feature evident in the original TTT diagrams is that the bainite curves (Figures 11 and 12) have flat tops; this means that there is an incomplete transformation at a given temperature and that the temperature must be reduced in order to achieve further reaction. This feature is related to what is known now as

phase diagram." The resulting representation, known now as a time-temperature-transformation (TTT) diagram, formed the basis of numerous studies, which today, have extended to all materials including, for example, polymers and the crystallization of metallic glasses. It led to the development of many kinds of dilatometric instruments that are now a standard feature of a well-founded metallurgical laboratory. But more so, the diagrams, because they dealt with constant temperature transformation, became the focus of theoretical studies on the nucleation and growth mechanisms of the phases that form in steels. A further tranche of theory, which admittedly has had limited success, was established to convert TTT diagrams into those appropriate for continuous cooling transformation. It also became popular to look at metallographic samples in their partially transformed condition so that morphology could be studied prior to its modification by impingement. There are a number of TTT diagrams in the original article, but those for steels containing chromium are

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<sup>\*</sup>E.S. Davenport and E.C. Bain: *Trans. AIME*, 1930, vol. 90, pp. 117-54.

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the  $T_0$  curve, which defines the limit of how much bainite can be obtained at a given temperature. It is the most important design criterion for modern bainitic steels, whose properties rely on transformation plasticity and which are used extensively in the automotive industries.

This brings us to one of the most important instinctive conclusions reached by Davenport and Bain. They were aware from the acicular appearance that the "bainite" was not related to pearlite and that it etched darker than virgin martensite. They could not resolve the carbides in those days but felt that there must be some cementite precipitation associated with bainite; after all, it was a little softer than martensite. The evidence in their possession led them to suggest that the allotropic change occurs in advance of the carbide precipitation. In other words, the transformation is like martensite, but the product soon afterward tempers to precipitate cementite.

To me, this is an incredibly clever piece of deduction, which accounted well for the diverse data they had collected given the limited experimental methods

available at the time. Of course, there has been a lot of trauma since this original proposal for the mechanism of transformation, but I think it is safe to believe that the mechanism stands, and indeed, it is only this mechanism that permits the quantitative design of steels.

There is one regrettable fact of history. I approached a number of eminent metallurgists (Morris Cohen, Harold Paxton) in the United States some decades ago to seek their help in accessing the original manuscripts and laboratory records of Davenport and Bain. Unfortunately, these seem to have been destroyed or lost. It would have been terrific to follow the minute details of the path, which led to the monumental work that is the 1930 article.

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# Transformation of Austenite at Constant Subcritical Temperatures

By E. S. DAVENPORT\* AND E. C. BAIN, TKEARNY, N. J.

(Chicago Meeting, September, 1930)

When annealed carbon, or low-alloy, steels are suitably heated the ferrite (alpha iron solid solution) and the carbide, of which they are composed, react together to form a single solid solution of carbon (and other elements) in gamma iron (austenite). This reaction may begin only at a certain minimum temperature called the eutectoid temperature. The first ferrite and carbide thus to react together do so in definite proportions known as the eutectoid composition. With further heating the original constituent that is present in excess is dissolved in the austenite until exhausted. Whether the excess constituent be ferrite (hypoeutectoid steels) or carbide (hypereutectoid steels) the procedure is much the same, and upon slow cooling the homogeneous austenite expels the excess of either (proeutectoid ferrite or carbide) until the eutectoid composition is reached. Thus the reaction upon heating is strictly reversed upon cooling and accordingly an equilibrium diagram of this process may be constructed.

Such an equilibrium diagram concerns itself only with the temperatures involved and with the proportions and compositions of the phases developed under conditions that suffice to permit equilibrium. Specifically it has no concern for the type or mode of distribution of these constituents nor with any extra-equilibrium conditions such as undercooling, which is almost universally encountered in metals. Actually, however, of great importance is the sluggishness toward equilibration caused by the not inconsiderable time involved in diffusion. Thus instead of the theoretical transformation point  $A_E$ , we find for a certain rate of heating or cooling the use of the designations Ar and Ac (transformation temperature found on cooling and upon heating). These figures obviously have no particular meaning except as measured and expressed for a definite heating or cooling rate, and represent the apparent temperature displacement caused by an inadequate time allowance.

In this paper are presented the results of a study of the time required for the transformation of austenite to ferrite and carbide at a variety of temperatures and also of the time required for the reaction austenite—martensite at the temperatures at which this reaction occurs instead of

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<sup>†</sup> Hunt Medallist, 1929.

the one first mentioned. In short, this study proposes the addition of the time factor to the iron-carbon diagram.

## TIME REQUIRED FOR TRANSFORMATION OF AUSTENITE

Some ideas as to the time required for the transformation of austenite have been offered by earlier investigators. Portevin and Garvin,¹ Chapin² and Lewis³ have observed the unexpectedly low rate of the reaction at temperatures in the vicinity of 300° C. (575° F.) for carbon steels, and DeLong and Palmer⁴ have described the same type of sluggishness in high-speed steel at its analogous temperature range in the vicinity of 600° to 650° C. (1100° to 1200° F.). Many years ago one of the present writers observed the slow transformation of austenite in a low-alloy steel cooled quickly to about 225° C. (440° F.) in hot oil. The specimen was immediately transferred to a Rockwell hardness tester but its hardness could not be measured accurately on account of the continuous expansion accompanying the transformation, which caused the needle to traverse the dial at a moderately rapid rate for several minutes.

It is well known that rapid cooling will undercool austenite for several hundred degrees prior to its transformation. It is equally well known that the degree of rapidity of cooling has a profound effect upon the nature of the product of the transformation. For example, a slow cooling is said to produce coarse lamellar pearlite while rapid cooling may produce troostite or even martensite. The present authors have adopted the viewpoint that any restricted portion of a piece of steel acquires a given structure upon transformation as a result (almost wholly) of the temperature at which transformation occurred. Obviously the temperature of transformation of this infinitesimal of austenite may have been determined by the rate of cooling of the whole mass, but it owes its final structure to the circumstance of its having transformed at a certain subcritical temperature. The specimen as a whole transformed at a variety of temperatures, perhaps, but if so its structure also covered a range of characteristics. In most cases, the rate of cooling of a specimen of steel may be the means of determining the temperature at which a given portion of the metal inaugurates its transformation. That the rate of cooling per se has any effect upon the product or velocity of the transformation, except by this indirect means, seems extremely doubtful.

<sup>&</sup>lt;sup>1</sup> A. Portevin and M. Garvin: Fundamental Investigation of the Influence of the Rate of Cooling on the Hardening of Carbon Steels. *Jul.* Iron and Steel Inst. (1919) **99**, 469.

<sup>&</sup>lt;sup>2</sup> W. R. Chapin: Properties of Some Steels in the Hardening Range. *Trans. Amer.* Soc. Steel Treat. (1922) **2**, 507.

<sup>&</sup>lt;sup>3</sup> D. Lewis: Transformation of Austenite into Martensite in an 0.8 per cent. Carbon Steel. Jul. Iron and Steel Inst. (1929) 119, 427.

<sup>&</sup>lt;sup>4</sup>B. H. DeLong and F. R. Palmer: What Happens when High-speed Steel is Quenched. Trans. Amer. Soc. Steel Treat. (1928) 13, 420.

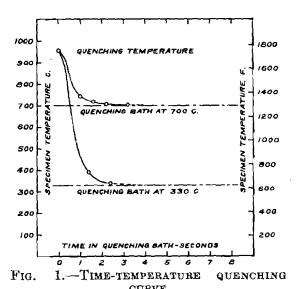
That this viewpoint is wholly tenable seems established by the results of the authors' investigations, which were all obtained from comparatively small specimens that could be rapidly cooled as pure austenite to any desired temperature and then given no choice but to transform at that constant temperature. The temperatures for transformation that were studied cover the range from the lower critical down to room temperature. The general trend of the effect of transformation temperature upon the time of transformation and upon the nature of the product was worked out first in detail for a single steel. This necessitated study at a great number of temperatures, and to reduce the task to practicable dimensions other steels were studied less thoroughly and the intermediate temperature effects were interpolated on the basis of the more minutely observed behaviors encountered in the first representative steel. The need for this procedure will become evident in the following discussion.

## METHODS OF INVESTIGATION

In order to observe the progress of austenite transformation at any definite temperature it is necessary, obviously, to cool the properly heated specimen rapidly to the temperature for study and then to main-

tain it at that temperature within narrow limits. The quenching to this subcritical temperature must be rapid enough to preserve the austenite essentially unchanged down to the observation temperature, and to prevent transformation from occurring at any temperature above (or below) the one chosen for study.

Specimens.—These restrictions demand the use of (1) thin specimens with high surface-to-mass ratio and (2) a quenching bath of high cooling power



automatically controlled at constant temperature. For all practical purposes these conditions were obtainable. Steel specimens about 0.060 in. thick were found to cool rapidly enough in a molten lead bath. They were sufficiently thick, on the other hand, to withstand Rockwell hardness measurements with inconsequential error. Therefore the various steels were obtained in the form of flat strip, usually about 1/2 in. wide. Such strip was suitable for microscopic examination and

rigid enough for the dilatometric investigation described below.

Quenching Mediums.—Information from various sources led to the belief that molten metal baths would be best suited to this investigation.

For the lower temperatures the lead bath was alloyed with bismuth to form the eutectic composition, which remains molten down to about 135° C. (275° F.). To check the cooling rate of the flat specimens, some tests were made to discover the time-temperature behavior of the quenching. Thermocouples welded to specimens sufficed; other thermocouples of such dimension as to be thermally similar to the specimens were also quenched and their behavior observed. Fig. 1 illustrates the cooling rate of the lead quench at two representative temperatures. In the light of the subsequent investigations the quenching rate appears in general more than sufficient to prevent any part of the transformation from occurring at temperatures intermediate between heating temperature and constant bath temperature, the only exception being in the case of one or two steels in the vicinity of 570° C. (1000° F.). It may be assumed that the specimens transformed only slightly or not at all at the temperature of most rapid action during the time of temperature drop. This point will become more apparent as the results are examined.

# Estimating Progress of Transformation

When steel transforms, a number of properties are changed. important property that is radically changed is the magnetic permeability. While the permeability is somewhat different among the products of the austenitic transformation at different temperatures, yet the order of magnitude of the permeability is entirely different as between austenite and the products of transformation. Therefore the decrease in austenite and increase in ferrite could be evaluated by observing the increase in permeability as the reaction proceeded. This method was actually utilized in somewhat similar work.<sup>5</sup> Volume changes also occur, which are characteristic for the austenite to ferrite change. Hence buoyancy evaluations might be continuously registered as the specimen undergoes change in the metal bath. Characteristic hardness changes result from transformation and, while somewhat complex, could be used to evaluate the progress of the transformation. In this case indentations with a uniform pressure might be made in the specimen at intervals and their depth interpreted later.

On the basis of practicability, two methods were used to estimate the progress of the reaction, one for the higher constant temperatures and another for the lower. Both methods were employed for some intermediate temperatures, providing thereby a check on their accuracy.

So far as temperatures from the lower critical (eutectoid) down to about 300° C. (570° F.) are concerned, the progress of transformation may be followed by a method of considerable dependability and directness. It depends upon subsequent microscopic examination and therefore may be carried out deliberately with no necessity of continued obser-

<sup>&</sup>lt;sup>5</sup> D. Lewis: Loc. cit.

vations of any manifestation at frequent intervals. By preparing a considerable number of small specimens the distribution and extent of austenite remaining after any length of time can be rigidly fixed and preserved for later evaluation. While austenite transforms to characteristic martensite upon quenching rapidly into a bath of cold water, it never forms martensite when it transforms in the temperature range down to 300° C. (570° F.), producing, instead, some form of pearlite or troostite. Hence, if a series of small specimens are quenched to the desired temperature in the molten metal bath and then, one by one, at suitable time intervals are removed quickly and quenched into water, the austenite unchanged at intermediate temperature will be fixed and preserved as martensite. Subsequent microscopic examination will then reveal in sharp contrast the progressive loss in austenite and gain in transformation products. The utterly different etching characteristics of martensite and the products of elevated temperature transformation serve to permit the most definite sort of area estimation. Such a series of specimens shows, for the short time in the bath of observation temperature, pure martensite, and for the very long times, pure pearlite or troostite, as the case may be. Intermediate times result in the expected mixtures in adequately sized areas for accurate planimetric estimation.

The specimens removed from the intermediate bath prior to any transformation are, incidentally, fully hard after the water quench (i. e., Rockwell 56 to 65, depending upon composition) whereas those removed to the water after considerable transformation has occurred are increasingly soft, reaching finally the normal hardness of the transformation product. Thus both hardness and structure furnish a clue to the procedure of the decomposition of austenite.

The second method used for the lower temperatures depends upon the increase in volume of any steel upon transformation to troostite or martensite as reflected by length change. The authors are aware not only that volume changes are slightly affected by shape of specimen but also that the volume change is not necessarily uniformly reflected in linear change in all dimensions. Indeed, the thickness of flat disk specimens actually decreases with volume increase! However, it has been established satisfactorily that length changes in long slender specimens of constant cross-section follow reasonably closely the transformation in the course of expansion. The method is not so precise in terms of quantitative estimation as the first method, but indicates with considerable fidelity the inauguration and completion of the transformation. The checking of the expansion against the microscopic appearance at intermediate temperatures provided evidence of excellent agreement in all steels save one (steel B) and even there the discrepancy was not serious.

To carry out the method of employing length change to indicate continuously the progress of transformation, some skill and dexterity is required. The hot specimen, heated to dissolve the carbide completely, must be removed from the furnace with heated tongs, attached to the dilatometer and immersed in the bath before proeutectoid constituents have time to separate or any decomposition occurs as a result of the slight air cooling, which, of course, is unpreventable. Frequent tests showed that this was accomplished in these investigations. (It will be seen that the time of appearance of the proeutectoid constituent was observed and recorded.)

The dilatometer used is illustrated in Fig. 2. It is similar to the one used by Bain and Waring<sup>6</sup> and by Grossmann,<sup>7</sup> but an extra precaution

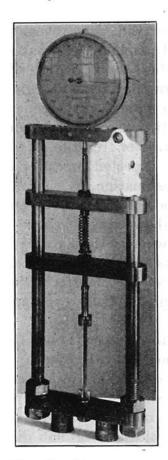


Fig. 2.—The Quenching dilatometer.

was necessary. The dial readings actually represent only the difference in expansion between the dilatometer fittings and the specimen. To ensure the accuracy of the expansion values it is necessary to reduce the length change in the dilatometer side rods substantially to zero. This was accomplished by holding the dilatometer in the molten metal bath until it was in thermal equilibrium (i. e., conducting away heat at a constant rate and with a constant thermal gradient existing). For inserting the specimen the dilatometer was raised in the bath momentarily and then replaced before significant temperature changes resulted. The more nearly the specimen retained the furnace temperature and the more nearly the dilatometer retained the thermal conditions set up by the bath, the more immediately and accurately would the dial readings reflect the true conditions in the specimen. As already stated, the instances wherein the steel began transforming within 2 or 3 sec. probably are not without some slight error.

In quenching the specimens to temperatures below the freezing point of the lead-bismuth bath, a large volume of water was used at 71° C. (160°F.) and at 15° C. (60°F.). The transformation time,

or at least the time for substantially complete transformation at such low temperatures, is too short to be measured very accurately. It has been shown that not only is some austenite retained permanently after low-temperature quenches, but that the last traces of austenite to transform under such conditions do so at an extremely slow rate. This paper does

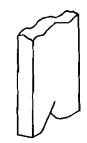
<sup>&</sup>lt;sup>6</sup> E. C. Bain and W. S. N. Waring: Austenite Decomposition and Length Changes in Steel. *Trans.* Amer. Soc. Steel Treat. (1929) 15, 69.

<sup>&</sup>lt;sup>7</sup> M. A. Grossmann: Discussion of paper by Bain and Waring. *Ibid.*, 90.

not concern such behaviors of the last traces, but confines itself to the estimation of the major portion of the austenite, which does transform. It is believed that the apparent end of reaction time as observed here represents the transformation of about 99.5 per cent. of the austenite undergoing transformation (exclusive of that retained permanently).

It has already been pointed out that the specimens must be introduced into the dilatometer and then submerged into the quenching bath very quickly. To aid in accomplishing this, each end of the specimen was broadly notched and these polished notches engaged similar notches in the fixed and movable part of the dilatometer set at right angles to the flat specimen (Fig. 3). In a sense, therefore, the specimen was self-

aligning. The relation of the specimen to the seats in the dilatometer at the point of engagement was actually similar to that of adjacent links in a simple chain. Precision of the readings was improved by attaching a small vibrator to the dilatometer. The vibrator consisted of a signal buzzer operated from a battery (Fig. 2).



## STEELS CHOSEN FOR STUDY

The steels chosen for study were representative materials of low alloy content and of an intermediate content of manganese; they form a variable carbon series and a manganese series. A typical high-carbon steel with a little chromium, such as that used in razor-blade strip, also was investigated. To present one example of a high-alloy material, standard stainless cutlery steel was explored in a somewhat less detailed manner.

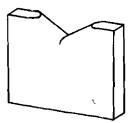


FIG. 3.—ENGAGE-MENT OF SPECIMEN IN DILATOMETER SEATS.

The analyses of the seven steels investigated are given in Table 1.

Table 1.—Analyses of Steels Investigated

Steel <sup>a</sup>	Carbon, Per Cent.	Manganese, Per Cent.	Silicon, Per Cent.	Sulfur, Per Cent.	Phosphorus, Per Cent.	Chromium Per Cent.
	1.13	0.30	0.171	0.015	0.026	
В	0.78	0.36	0.160	0.048	0.036	
$\mathbf{C}$	0.54	0.46	0.198	0.041	0.048	
D	0.50	0.91	0.131	0.041	0.046	
${f E}$	0.64	1.13	0.094	0.030	0.048	
${f F}$	1.17	0.30	0.180	0.033	0.026	0.26
$\mathbf{G}$	0.35 - 0.40	İ				12-14

<sup>&</sup>lt;sup>a</sup> Steels A, B and C constitute the carbon series; C, D and E constitute the manganese series; F is a razor-blade steel and G is cutlery stainless steel.

Steel B was studied more minutely than any of the others. In the course of observing its behavior at many temperatures selected at close

intervals, not only was skill and experience acquired but the general trends of the temperature effect were observed in sufficient detail to warrant reducing the number of temperatures selected for investigating the other steels. The study of this steel involved 152 separate microscopic examinations and the plotting of 13 expansion curves. It would not have been practicable to examine all the steels in such detail.

## RESULTS OF INVESTIGATIONS

The behaviors investigated may be designated as

- 1. Time involved in transformation.
- 2. Hardness of the products as influenced by temperature of transformation.
- 3. Structures resulting from transformation at the various temperature ranges.
  - 4. Effect of carbon and alloys upon transformation time.
  - 5. Retention of austenite at lower temperature ranges.

## Time Required for Transformation

As outlined above, the progress of the transformation was followed by two methods. When the microscopic appearance was used as the method of estimation the nature of the product was simultaneously observable. In this case enough specimens were employed to give some definite notion of the velocity of the reaction at different times. By interpolation the time required for certain definite fractions of the austenite to transform was estimated. The direct evidence from the specimens held in the molten bath for different lengths of time was recorded in terms of the percentage of austenite unchanged, pearlite or troostite already formed and proeutectoid constituents, if any. Subsequently this information was condensed graphically by the use of symbols (Fig. 14) in circles located on a time-temperature system of coordinates. Fig. 4 shows such a chart subsequently discussed in detail.

Carrying out the expansion method involved plotting the time-length change curves. The total expansion that occurred was taken to correspond with complete transformation and the times required to permit definite fractions of this total expansion were read off this graph as the time of fractional conversion of austenite. In this manner the expansion data at low temperatures were secured and plotted (as in the lower portion of Fig. 4) as derived from a family of expansion curves like that shown in Fig. 5. It might be pointed out that the bands of increasing width of Fig. 4 are plotted to a definite scale of expansion and represent the beginning of the transformation, the 25 per cent. transformation, the 50 per cent., the 75 per cent. and the concluded transformation as evidenced by the expansion.

From such charts as the one in Fig. 4 were prepared the summary curves for the various steels, Figs. 6 to 12 inclusive. All the data, in detail,

from which the summaries were prepared are shown only for steel B, it being assumed that the chief interest lies in the summary and the inclusion of so many charts would require too much space.

It should be mentioned, perhaps, that there is necessarily some vagueness concerning the exact instant of the beginning of the transformation and its end. (In all probability the curves of all such processes may actually be asymptotic at the conclusion.) It may be said,

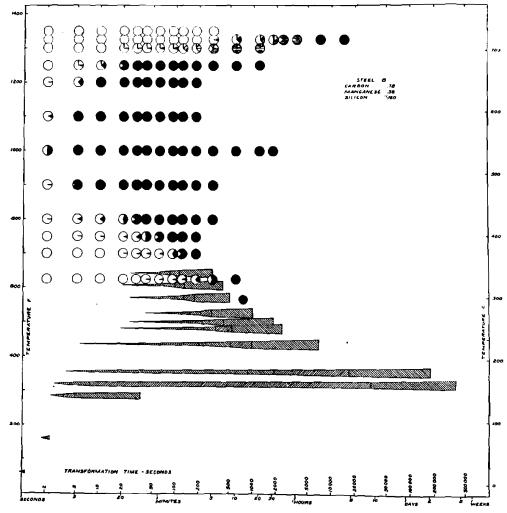


Fig. 4.—Typical data chart for transformation time and structure (steel B)

however, that the time point selected as representing the inauguration of the transformation marks the decomposition of less than 0.5 per cent. of the austenite, and that the time indicated as the end of the transformation designates that not more than 0.5 per cent. of the ultimately transforming austenite remains.

In the case of steels of composition remote from the eutectoid, the proeutectoid constituent separates out at subcritical temperatures: but only at temperatures a few hundred degrees Fahrenheit below the critical. At temperatures below this range, this does not occur. The time of this

proeutectoid separation is shown for the hypoeutectoid steels; the actual estimation of proeutectoid carbide is less easily made, and is not shown. In all cases, the lower the temperature of the transformation the smaller is the volume of excess constituent (ferrite or carbide) precipitated prior to the general decomposition.

It may be regarded as unfortunate that the abscissas of the various charts show time on a logarithmic scale. Actually this is practically

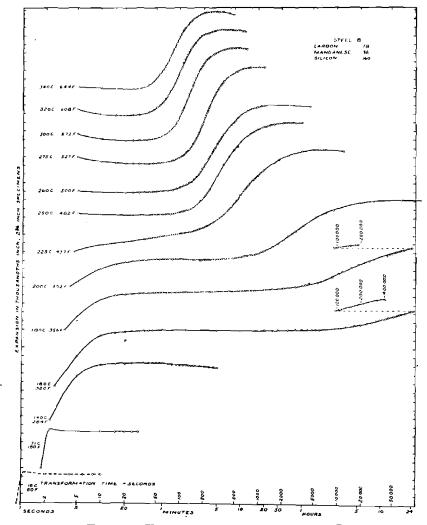


Fig. 5.—Expansion curves for steel B.

unavoidable because of the great disparity in rates of transformation at the various temperatures. Indeed, the transformation may require over 100,000 times as long an interval at the temperature range of slow action as at the temperatures of rapid reaction. If a linear scale were adopted, obviously no detail could be shown in the short time intervals.

For all the steels the transformation time graphs (Figs. 6 to 12) take the roughly approximate form of S-shaped curves. This circumstance is seemingly highly characteristic of all hardenable steels. The precise location of the S curve depends upon composition, but even the high alloy steel shows the same trend. There are two temperature ranges of

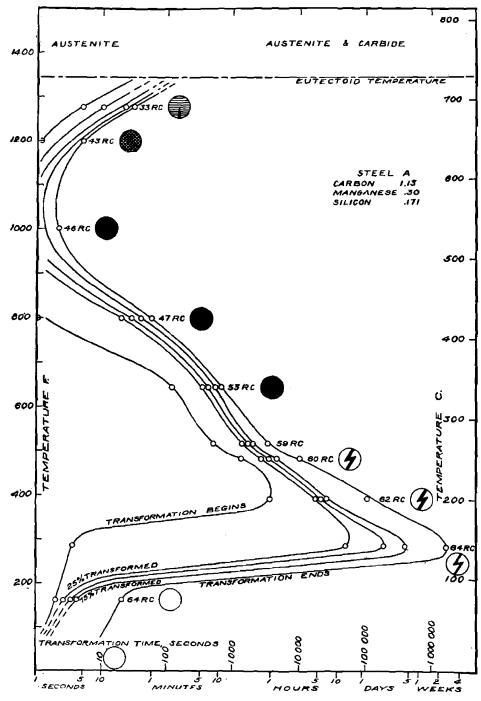


FIG. 6.—SUMMARY CHART FOR STEEL A.

very rapid transformation; one at about 550° to 600° C. (1000° to 1100° F.) and the other at low temperature not exceeding about 150° C. (300° F.). For high-alloy steels these ranges may be somewhat different, depending again upon composition. This circumstance of the two

ranges of rapid transformation throws new light upon the significance of the so-called A' and A" points. Strictly speaking, there are no actual

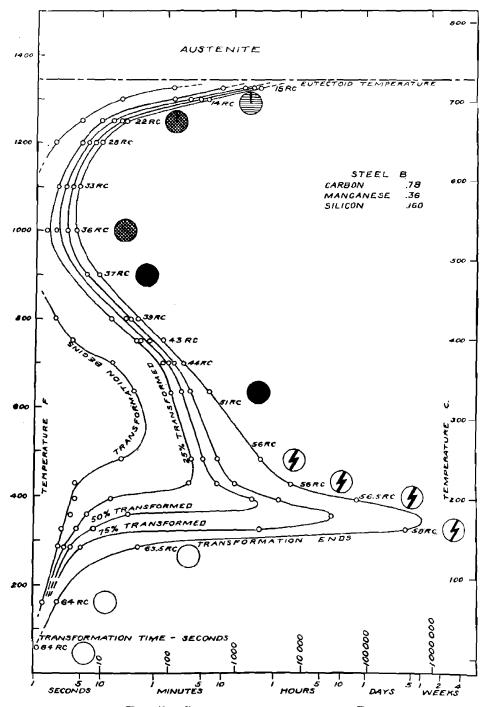
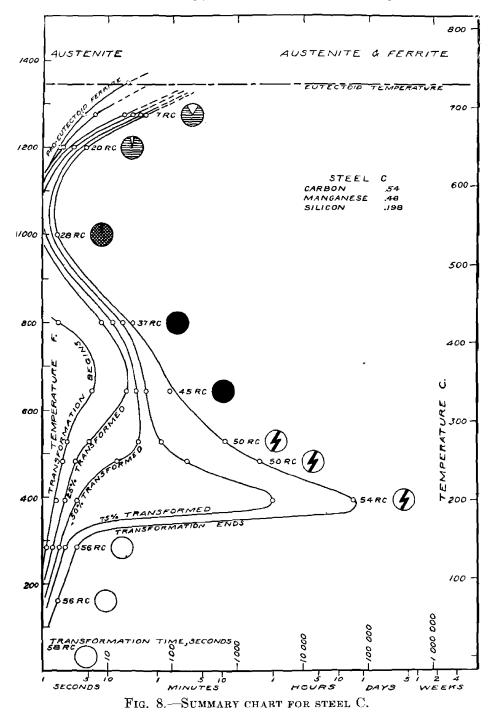


Fig. 7.—Summary chart for steel B.

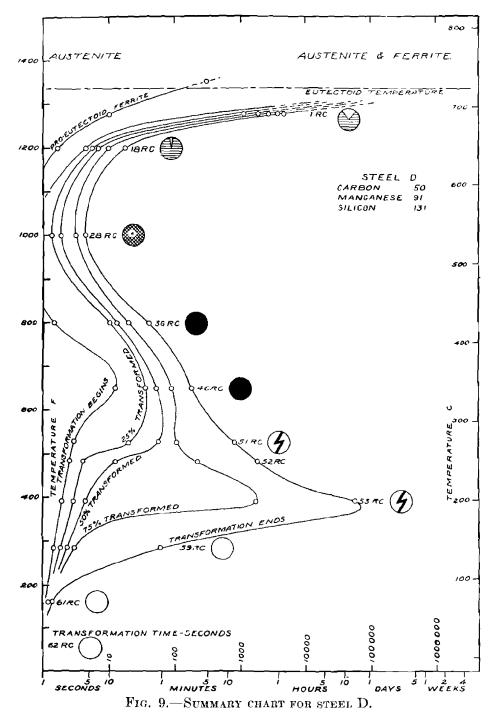
"points," but with any cooling at moderate rate the metal will be in the upper range of high transformation velocity sufficiently long to transform; if, however, the quenching rate is sufficiently high to cool the steel through this range unchanged, then so slow is the reaction at the next

lower temperature range that in general the austenite must reach the second region of high transformation velocity, there to transform in a different manner. Obviously, certain rates of cooling will permit a



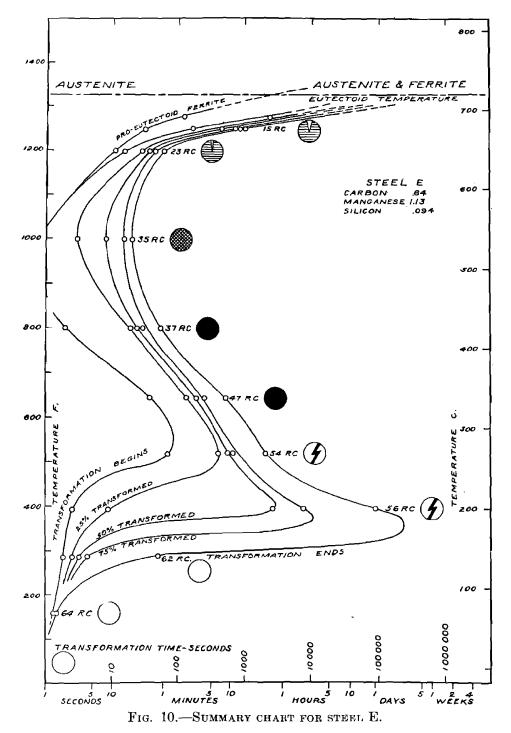
portion of the austenite to transform (the innermost region, for example) at A' and the remainder will only react at A". The "split" transformation takes on a definite significance in the light of these rates of transformation at constant temperatures.

It seems more than probable that the transformation time for certain high-alloy steels that harden completely in oil or air may be infinitely



long at certain temperatures. At any rate, nearly a month at 200° C. (390° F.) caused only a beginning of transformation of the austenite of the stainless cutlery steel G, although the specimen when cooled to about 100° C. (200° F.) hardened thereafter almost instantly to full hardness value. In this connection it is interesting to read the paper by DeLong

and Palmer<sup>8</sup> on what happens when high-speed steel is quenched and the discussion which the paper called forth.



In the range of temperature from the eutectoid down to about 500° C. (930° F.) the time of transformation appears to decrease with either increasing or decreasing carbon as it departs from the cutectoid

<sup>&</sup>lt;sup>8</sup> B. H. DeLong and F. R. Palmer: Loc. cit.

composition, which appears to be the most sluggish toward change. In this range of temperature, manganese retards the reaction markedly.

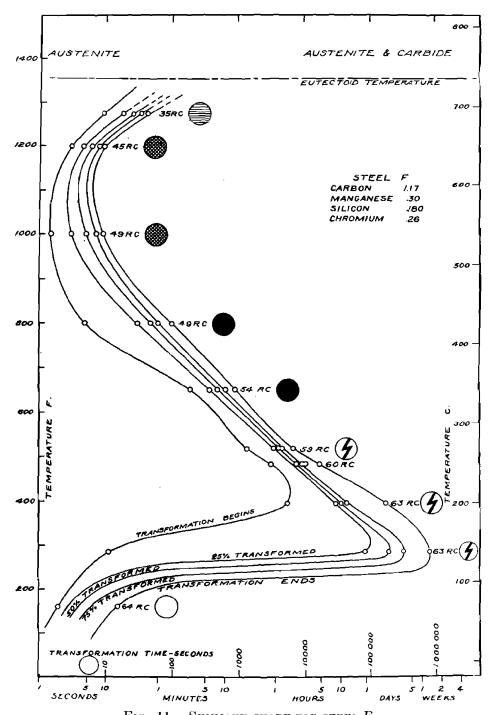
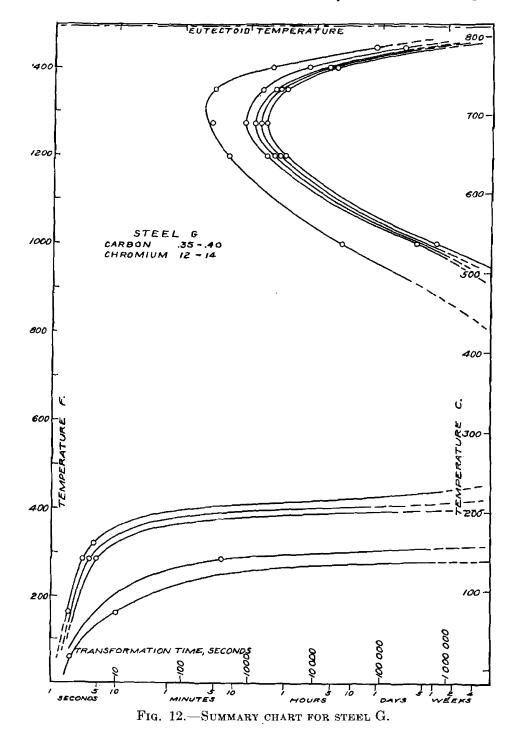


Fig. 11.—Summary chart for steel F.

At the lower temperatures of transformation both carbon and manganese have the definite effect of decreasing the rate of transformation. This effect is particularly evident in the time required for the beginning of the reaction. The temperature of maximum time lag prior to incipient transformation is lowered both by carbon and manganese.



Even the small amount (0.26 per cent.) of chromium present in steel F seems by comparison with steel A to retard the reaction of the austenite, especially at elevated temperatures where the transformation is most rapid. Fig. 12, of the stainless steel G, shows how the S-type curve

actually persists even when the chromium has caused the steel to become so sluggish as to render its study entirely impractical in some ranges. In determining the severity of practical quench necessary for hardening a steel, the maximum rate of transformation that occurs at 600° to 700° C. (1100° to 1300° F.) is the real criterion. Once the metal cools below this temperature range, it is most likely to harden upon subsequent cooling. It is apparent, therefore, that steel G should be an air-hardening steel.

# Hardness of the Transformation Products

The curves of Fig. 13 show the hardness (at room temperature) of the various transformation products of the several steels as developed over

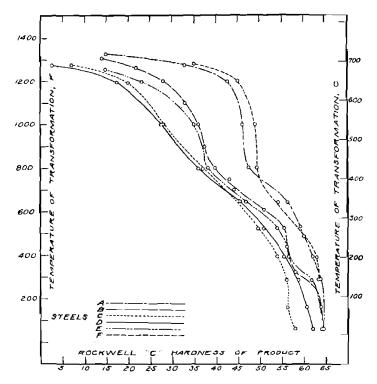


Fig. 13.—Rockwell hardness of completed transformation products.

the entire temperature range. As would be expected, the lower transformation temperatures produce structures that are greatly harder than the products from higher temperature of transformation. The hardness does not vary uniformly with the temperature of the action, but seems to vary in a characteristic manner. This may be explained on the basis of the time effect. Thus, when the transformation is very slow, the first austenite to transform is subjected to the drawing or tempering action of the bath over the entire time required for the last fragments of austenite to react. Hence we should find disproportionate softness in the products from temperatures of slow transformation and comparatively greater hardness in the product that transformed rapidly. A comparison of the

hardness curves (Fig. 13) with the summary curves will show the existence of this relationship.

It is important to bear in mind that the figures as plotted on the hardness curves (Fig. 13) and as noted on the summary charts are representative of the hardness of the product of the *just-completed* transformation. The hardness of any actual specimen permitted to remain in the molten bath after the austenite has completed its transformation will gradually fall, on account of coalescence of the carbide. The lamellar pearlite gradually spheroidizes and the products of finer carbide distribution similarly coalesce at rates depending upon the temperature. This action is slow in comparison with the rate of the decomposition of austenite at higher temperatures.

In this connection it may be well to mention that the hardness of the successively water-quenched microscopic specimens withdrawn from the metal bath at intervals constitutes also an excellent check on the microscopic estimation of the progress of the decomposition of the austenite. Specimens removed from the transforming temperature bath and quenched in water before much action has occurred possess nearly full martensitic hardness. Those removed after the transformation has occurred are, as would be expected, very much softer.

A set of such hardness curves with hardness plotted against time at constant temperature was made for each steel studied. The transformation time may almost be read from these curves alone.

## Structures Resulting from Transformation at Various Temperatures

A discussion of structures in steels almost unavoidably involves the use of certain well established names, which have their origin in microscopic appearances. That these names are difficult to assign in the present specific cases arises from a number of circumstances, some of which are general and some of which apply particularly to the present study. The structure as studied in the microscope is merely the appearance of a metallic surface after the devastation of an acid corrosion attack has occurred. Under vertical illumination the gradation of reflecting power of such surfaces from point to point depends upon a variety of circumstances not well understood. Where two or more phases of resolvable dimensions are present, the inferences may be drawn with some assurance, but when such conditions do not obtain (as with all lowtemperature transformations in steel) the nature of the structure must remain obscure after microscopic examination. In spite of this undeniable physical consideration, the authors have attempted to follow the custom and to name the structures found in accordance with the traditional conventions.

Some of the types of ferrite-carbide association obtained by the present heat treatments do not fit in well with the usual martensite-

troostite-sorbite-pearlite series. In accord with the suggestions made by both Hoyt and Sauveur, the name sorbite has not been used at all. For many years the authors have believed that the "nodular troostite" developed by quenching at an intermediate rate was actually fine pearlite. Since the presentation by Lucas<sup>10</sup> of a similar view, it seems clear that the product of transformation at the constant temperature which forms this particular microscopic appearance should be called pearlite, or more specifically, fine pearlite.

The etching characteristics of several zones of quenching temperatures can actually be recognized after some practice, but it has seemed sufficient to name all the entirely unresolvable, 11 dark-etching products

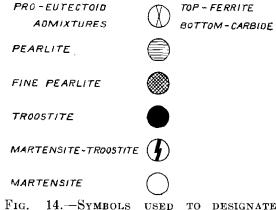


Fig. 14.—Symbols used to designate structures on all charts.

"troostite." The completed transformations forming troostite always possess the extremely rapid and dark-etching characteristics but vary somewhat in appearance with the temperature of formation and carbon content. A soft and vague acicular aspect may be seen with light etch, but the rate of attack (e. g., in 2 per cent. alcoholic nitric acid) alone would suffice to differentiate this constituent.

At lower transformation temperatures the product etches more slowly and the darker needles are clean-cut and definitely acicular. Even here, however, a brownish coloration shows that the product is not true martensite. To specimens of this intermediate appearance the name martensite-troostite has been given for convenience. When the slowest-etching acicular state of affairs was evidenced, the name martensite was used. Actually, if an extraordinarily severe etch is applied to a truly martensitic specimen, the final appearance is somewhat similar to that of the martensite-troostite group, but even then experience would enable one to distinguish between the two. It was most satisfactory to etch an entire series in a holder at one time, so that the conditions for all were identical as to time, temperature, etc. The authors wished to use numbers or letters to designate products of transformation but this seemed still more artificial and tedious for the reader and accordingly

<sup>&</sup>lt;sup>9</sup>S. L. Hoyt: Metallography. Pt. 2. Metals and Common Alloys. New York, 1920–21. McGraw-Hill Book Co.

A. Sauveur: The Metallography and Heat Treatment of Iron and Steel. New York, 1926. McGraw-Hill Book Co.

<sup>&</sup>lt;sup>16</sup> F. F. Lucas: Structure and Nature of Troostite. *Bell System Tech. Jul.* (1930) **9,** 101.

<sup>&</sup>lt;sup>11</sup> Unresolvable so far as individual carbide particles are concerned.

this attempt to adhere both to fact and convention was decided upon. It is suggested that the reader substitute for the names used here any that he finds more convenient for the structures designated. No defence for the present names is offered other than that of expediency. The names chosen by the authors are as follows; the symbols are shown in Fig. 14:

- 1. Pearlite—easily resolvable lamellar carbide-ferrite eutectoid structure.
- 2. Fine pearlite—lamellar eutectoid structure resolvable only at highest powers, which forms by the nodular process.
- 3. Troostite—dark-etching unresolvable appearance, which forms by somewhat acicular development and not by radial or nodular growth.
- 4. Martensite-troostite—the structure that forms by distinct acicular procedure and retains acicular markings, but etches much more rapidly than martensite and less rapidly than troostite.
- 5. Martensite—the structure of full-hard quenched steel, which etches slowly and shows acciular markings. By virtue of its slow attack it is always brilliant white by contrast with the other products of transformation.

The typical appearance of the end products of austenite transformation are shown in Figs. 15, 17, 19, 21 and 22. In the order mentioned they are of pearlite, fine pearlite, troostite, martensite-troostite at its lowest temperature range (just distinguishable from martensite) and martensite-troostite at the highest range of formation. To illustrate more clearly the mode of development of the first three constituents, photomicrographs of the same constituents as partly transformed from austenite are also included. Opposite the corresponding photomicrographs of completed transformation products will be found Figs. 16, 18 and 20, showing the partly transformed austenite resulting from the interruption of the transformation at an intermediate stage. Actually the white background of the photomicrographs is martensite but was austenite at the moment of the quench from the lead bath into water. The specimens were deliberately etched so as to show no detail in the background, thereby simulating more nearly the ideal conditions, which would obtain if one could observe the transformation as progressing at the temperature of transformation. Fig. 22, of the martensite-troostite constituent transformed at the highest part of this temperature zone, resembles more closely the pure troostite, whereas the structure of Fig. 21 is very near that of true martensite. However, the etching rate is sufficiently different from that of martensite to warrant a different classification.

To illustrate further the basis for naming as fine pearlite that certain constituent which forms by nodule growth with roughly radial markings, Figs. 23 and 24 are introduced. These photomicrographs were made at about the limit of resolution of the microscope ( $\times$  2500) and show clearly

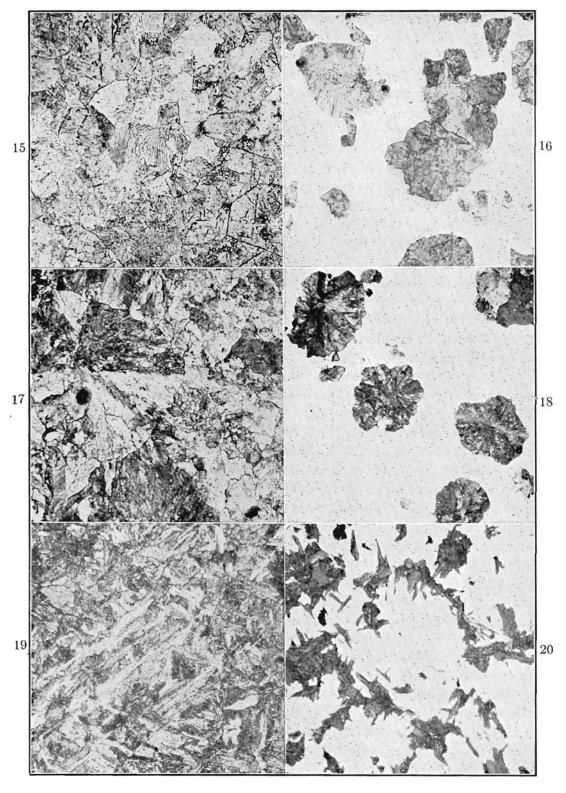


Fig. 15.—Typical pearlite.  $\times$  500. Fig. 16.—Pearlite partly formed.  $\times$  500. Fig. 17.—Typical fine pearlite.  $\times$  500. Fig. 18.—Fine pearlite partly formed.  $\times$  500. Fig. 19.—Typical troostite.  $\times$  500. Fig. 20.—Troostite partly formed.  $\times$  500.

the distinctly lamellar characteristics of the product. Each figure shows a large proportion of this clearly lamellar condition and even the remainder suggests this condition, as though the plane of the polished section had been too nearly normal to the lamellae to offer sufficient separation in the traces.

As has been pointed out earlier, at temperatures a few hundred degrees below the eutectoid, the transformation of the austenite is preceded by a separation of proeutectoid constituent if the composition of the steel is somewhat removed from the eutectoid carbon content. The magnitude of the proeutectoid constituent becomes less as the constant temperature of transformation falls lower, until at about 593° C. (1100° F.) no more ferrite or carbide separates and the steel transforms as a whole. In

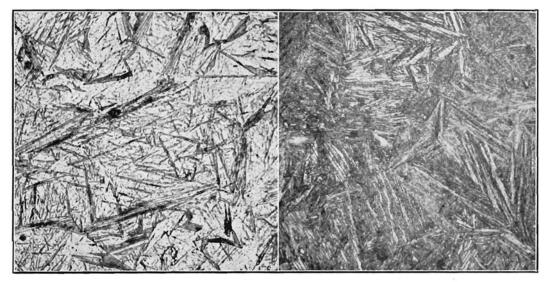


Fig. 21.—Martensite-troostite, low range.  $\times$  500.

Fig. 22.—Martensite-troostite, high range.  $\times$  500.

Figs. 25 and 26 are shown the structures of a hypocutectoid and hypereutectoid steel, respectively, as held for some time just below the critical temperature and then quenched. The constituent marking out austenite grain boundaries in the hypocutectoid steel is ferrite and in the hypereutectoid steel it is carbide. The quenching here took place at a time to prevent the formation of pearlite in the high-carbon steel, while Fig. 25 shows the transformation as having progressed sufficiently to form some pearlite. As a matter of fact, even substantially below the lower critical temperature, the reactions appear to take place somewhat normally in that no further procutectoid constituent separates after the eutectoid transformation begins, regardless of the amount of the constituent separated.

No photomicrographs of martensite are shown here; the appearance was precisely that of the hundreds of etched martensite photographs shown in many publications.

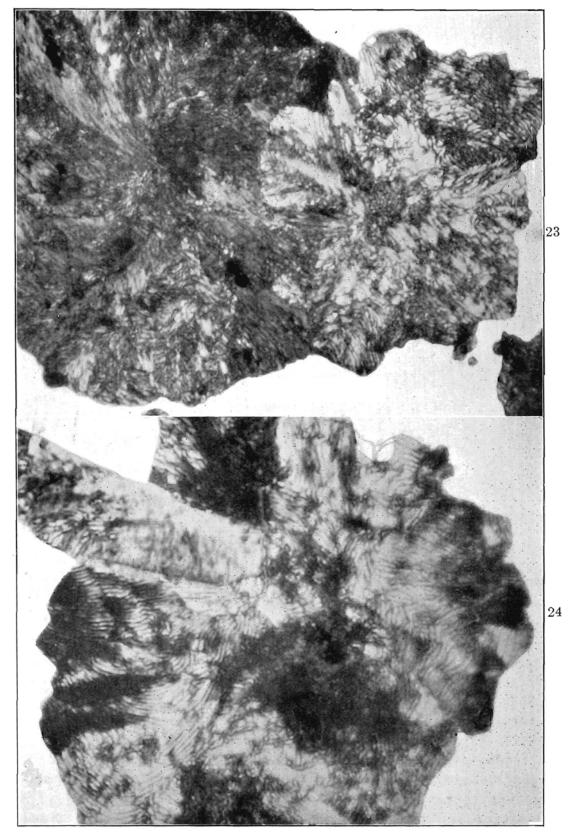


Fig. 23.—Fine pearlite.  $\times$  3000. Fig. 24.—Fine pearlite.  $\times$  3000.

It may be well to point out some of the characteristic differences between the transformation products of hypereutectoid and hypoeutectoid steels, although it must be admitted that the outstanding characteristic of the structures is their general similarity. Except in respect to the proeutectoid material, no significant difference exists between the pearlite and fine pearlite of the two classes of steels. In the formation of troostite there is one difference, which is marked. The troostite of low-carbon steels forms by the development of more distinctly rectilinear markings; the high-carbon troostite is less acicular and more ragged. These tendencies are most easily recognized in the partly transformed material

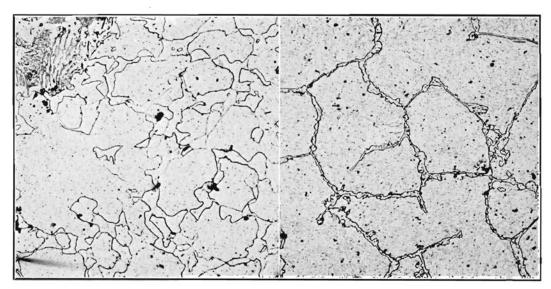


Fig. 25.—Proeutectoid ferrite. × 500.

Fig. 26.—Proeutectoid carbide. × 500.

but would not be overlooked even in the finished product. The photomicrographs shown are probably slightly more characteristic of highcarbon material than of the low-carbon.

In the formation of the product designated here as martensite-troostite, the tendencies described for troostite are practically reversed. The dark-etching "needles" are more perfectly rectilinear and more sharply defined in the higher carbon steels. The manganese content has surprisingly little effect upon the appearance of the transformation products.

In the investigation, some 600 specimens were examined microscopically, but it is believed that the 12 structures shown here are sufficiently representative to give an adequate survey of the effect of temperature of transformation upon the structure of the product. Furthermore, since the inauguration of this investigation, a publication

by Robertson<sup>12</sup> has treated the microstructural aspects of a similar study in an excellent manner.

## Retained Austenite

Under the heading Time Required for Transformation, the fact was stressed that the discussion of rates of decomposition of austenite did not deal with permanently retained austenite nor even with any austenitic transformation that was occurring so slowly that no measurable expansion was incurred in a few days at constant temperature. It seemed important, nevertheless, to estimate by means of the X-rays the conditions under which austenite was retained after transformation had appeared to cease. Such an estimation may not be carried out accurately, it is found, because martensite or martensite-troostite produces an X-ray diffraction pattern of such diffuseness as to make intensity comparison with the sharper austenite pattern very difficult. Still, some fair approximation may be made. In brief, the deductions are as follows:

- 1. No austenite was found in the products of transformation at temperatures above 180° C. (356° F.) in any steel.
- 2. Steel B retained a trace of austenite after transformation at 180° C. (356° F.) but the other steels contained no austenite unless they transformed at temperatures of 140° C. (284° F.) or below.
- 3. The amount of austenite retained was perhaps greatest after the water quench at 16° C. (60° F.) but very little more was retained than after the quench into water at 71° C. (160° F.); at higher constant temperatures the amount fell off rapidly.
- 4. The amount of austenite retained increased rapidly with carbon content, reaching about 20 or 25 per cent. in the high-carbon steels A and F and amounting only to a trace in steel C of low carbon content (0.54 per cent.).
- 5. Austenite may be definitely retained permanently in steels in which the ultimate transformation product is not martensite but one of the softer martensite-troostite structures.
- 6. The stainless cutlery steel, for all its great sluggishness, retained far less austenite than the high-carbon steel, presumably because of its low carbon content (0.35 per cent.). Carbon ranging from 0.50 to 1.20 per cent. is far more effective in increasing retained austenite than manganese ranging from 0.46 to 1.13 per cent.

## DISCUSSION OF RESULTS

The C-shaped curves for all steels resulting from plotting temperature of transformation (between eutectoid temperature and that of maximum time) against time required may be predicted from purely

 $<sup>^{12}</sup>$  J. M. Robertson: The Microstructure of Rapidly Cooled Steel.  $\it Jnl.$  Iron and Steel Inst. (1929) 119, 391.

physical-chemical considerations. The reaction time for transformation may be regarded as the summation of the time factors of two essential effects, "tendency" or "driving force" and ease of transformation or "facility," neither of which is linear with temperature. The former would tend to decrease the time rapidly at first with falling temperature, then more slowly. The other would tend to hold the time short at the temperature near the critical but to increase it enormously at lower temperature ranges. Obviously, the mutual effect would cause the typical minimum observed in the vicinity of 540° C. (1000° F.). second temperature of rapid transformation must be explained on the basis of some other consideration. There is no lack of sufficient differences in the nature of transformations at room temperature or thereabouts from which to construct theories. The two most entertaining ones are probably the negative "ferrostatic" pressure, which a hard surface product might set up to catalyze the reaction, and the fact that martensite, the product of low-temperature transformation, is one in which no carbon diffusion or migration takes place.

Considering the first, it might be reasoned that the softer products of the long-time transformation in which carbon may easily precipitate lacks hardness and strength to exert during its expansion any great outward force in all directions while a harder, low-temperature product could well accomplish this. Such a negative pressure would certainly aid the transformation of austenite, since by its transformations it expands considerably. Such autoaccelerating effects are found in other cases. It might be reasoned, in the second theory, that the time-consuming part of transformation is the carbide precipitation incurred thereby and if this could be eliminated wholly or in part the mere allotropic transformation could proceed very rapidly, since it involves only a slight atomic rearrangement essentially in situ. Since martensite has essentially all the carbon held in unstable solid solution, the migration of carbon is avoided and the change can be almost instantaneous. Possibly both theories bear upon the subject.

At any rate, an inspection of the structures resulting from transformation over the temperature range indicates clearly that at elevated temperatures the carbide precipitation is not lagging far behind the allotropic change at any point. As the temperature of transformation is lowered, the tendency for the alternate, and hence simultaneous, separation of carbide and ferrite disappears and instead the trend of the allotropic change to sweep across a grain ahead of carbide separation becomes more and more marked down to the martensite reaction. A logical intermediate case would be the fine pearlite of nodular origin proceeding from a comparatively few nuclei. In forming troostite, the allotropic change would occur just a little in advance of the carbide precipitation—enough to produce the "needles" or bars across the

austenite grains. This trend seems to grow stronger and stronger with lowered temperature, until finally in martensite little if any carbide ever separates.

The authors suspect that the final constituent designated as martensite-troostite first forms much in the manner of martensite but is subsequently more or less tempered and succeeds in precipitating carbon, depending upon how long the restricted area under consideration remained at the constant temperature. This is borne out by the similarity of some of these structures to those of lightly tempered pure martensite. The tendency toward a light gray (or brown) etching effect also suggests slight carbide precipitation subsequent to the allotropic change.

The length of time required for transformation over a considerable range of temperature was surprisingly long. The products of transformation at some of these unusual temperatures possess desirable physical properties. It is important, however, that steel thus treated be not withdrawn prematurely from the bath temperature to finish transformation at a rapidly falling temperature, for the austenite remaining will then transform wholly or in part to martensite, the admixture of which will impair some of the physical properties of the metal. In general, it is far better to raise the temperature and maintain it long enough to make certain that complete transformation at the more rapid rate has occurred.

The transformation rate for some of the high-alloy tool steels is so low that they may be retained almost indefinitely at certain temperature ranges in the austenitic condition. Apparently the temperature of slowest transformation is the one at which carbide will just barely precipitate from the quenched steel upon reheating.

#### ACKNOWLEDGMENTS

The authors gratefully acknowledge their indebtedness to Mr. J. J. B. Rutherford and Mr. E. L. Roff, of the Research Laboratory of the United States Steel Corpn., for skillful assistance in securing many of the data and constructing many of the charts.

#### DISCUSSION

M. A. Grossmann, Canton, Ohio. - This brilliant paper clarifies many of our ideas on the hardening of steel. Certainly it brings in new conceptions of the Ar' and Ar'' points, the transformations at the upper and lower temperatures below the critical.

The program notes this as a session on theoretical metallurgy, but I think we should bear in mind that this has very important practical aspects also. When we consider that the quenching of a piece of steel into a bath at 250° degrees, or a bath at 200°, requires in the one case some two weeks for the transformation of the steel, as shown by the authors, and in the other case a fraction of a minute, I think we can see that this has very important bearing on all of our heat-treating operations, and also our conceptions of these operations.

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- D. J. Demorest, Columbus, Ohio.—I have had more clarification of my mind this afternoon, as a result of this paper by Messrs. Davenport and Bain about the processes of hardening, than from anything I have ever read before.
- F. B. Foley, Philadelphia, Pa. (written discussion).—The authors of this paper are to be congratulated for their technique and for their clear presentation of the results of this study of a rather elusive problem. It immediately brings to my mind the work on critical rates of cooling by Portevin and Garvin and also the work of French and Klopsch. It shows that the microconstituents of steels cooled from above the critical temperature are all direct decomposition products of austenite and not successive derivations of austenite through a series of transformations involving the traditional descent through martensite, then troostite, then sorbite, and, finally, pearlite. This latter series of transformations is produced in reheating austenite or martensite and is therefore identified with drawing or tempering. Two interpretations were possible of the split transformation which Portevin and Garvin found to produce a mixture of troostite and martensite: (1) that the troostite was produced as martensite at the higher transformation temperature and was drawn during the subsequent cooling to troostite, and that the martensite was the result of the lower temperature transformation directly from austenite which had escaped transformation at the higher temperature; (2) that the troostite was produced directly from austenite at the higher temperature of transformation and the martensite directly from austenite at the lower temperature of transformation. The present work shows the latter to be true. The method used by the authors discloses the mode of "delayed quenching," in which pieces may be withdrawn from the furnace and permitted to cool for a period of time in the air and then cooled rapidly. It suggests many variations in this process involving halting the cooling and retaining the piece at a particular temperature for a length of time and then quenching to produce a homogeneous structure. It is not possible in sustained cooling, except at speeds equal to or faster than critical rate, to produce a homogeneous structure, because the time at any particular temperature is not sufficient to enable the complete transformation at that temperature to take place and the subsequent cooling is not rapid enough to prevent further transformation at the lower temperatures. One would suppose, however, that further transformation at lower temperatures following the establishment of, let us say, fine pearlite would be very sluggish and that the rate of cooling of the fine pearlite, within reason, may not be a factor of considerable importance.

Of course, referring to the speed of transformation, the authors establish speeds of transformation of austenite to a particular constituent. Apparently, the rate of reaction in the austenite to pearlite transformation, which occurs at a moderately high temperature, is rapid and so is that from austenite to martensite at a very low temperature. The reaction rate producing intermediate microstructures at intermediate temperatures is very slow. This satisfactorily accounts in a large measure for the split transformation which occurs at slightly subcritical rates of cooling. In connection with the question of interrupted coolings from above Ac, it may be worth while to call attention to the fact, which has been observed, that when the cooling of pieces is halted in the region of the first transformation and then reheated, to say 1200° F., but below the Ac, the product has a fairly high tensile, strength but a comparatively low elastic limit, which may be raised by subsequently drawing the piece. This suggests that interrupted coolings are dangerous, unless intelligently and carefully controlled as to rate, temperature and time.

The portion of the paper dealing with nomenclature is rather interesting. Austenite is certainly a distinct entity and so are pearlite and martensite, though in lesser degree. Troostite, as the authors point out, has distinct etching characteristics—it etches darker and faster than martensite. Sorbite is discarded, yet in some steels

there is a condition recognized by many in the industry as sorbite. In certain nickel and nickel-chromium steels, for example, there is a condition produced by oil quenching and drawing at about 1200° F., in which the steel is fibrous, has excellent physical properties and gives high notched impact values. The microstructure is quite uniform and unlike that of any of the constituents described by the authors and one commonly called sorbite. For their purposes the names used by the authors are probably adequate to describe the structure, but it would be a distinct disadvantage to abandon the name sorbite, particularly since it is not clear that such a structure may not be produced at some intermediate temperature not studied in this work.

D. Lewis, Bridgeport, Conn.—The work that Messrs. Davenport and Bain did to produce their paper must have been colossal.

There are all sorts of things I should like to discuss, but I will keep to the theoretical discussion at the end, which is perhaps most interesting. Two explanations are put forward for the lower or Ar" point at which martensite forms. One is that a negative ferrostatic pressure is produced owing to expansion when austenite forms; the other one is that at the upper critical range the constituent separating is ferrite, and before it separates, diffusion of carbide is necessary and that takes some time and results in considerable slowing down of the reaction as the temperature falls, but that at the lower critical point there is no diffusion of the carbide and the alpha to gamma change takes place, leaving the carbide in situ.

Both explanations are interesting, but I feel sure neither is complete, and we have not yet found the real explanation of what is happening. I do not think that the ferrostatic pressure theory can hold very well, because it is difficult to understand why it should take effect at the particular temperature range where that change takes place. The author has suggested that it is because the martensite at that temperature is rather stiff and will not deform. But, on the other hand, the product is incompressible at higher temperature ranges, and should still produce a negative ferrostatic pressure.

I think the other explanation is much nearer the mark; that is, that the martensite change is a change from gamma to alpha in which the carbide does not diffuse. But there is one serious difficulty that I shall point out, with the hope that the authors will do more work and get nearer to the explanation.

I will refer to Fig. 6 in the paper. At temperatures above 1100° F. the authors obtained pearlite or nodular pearlite but below they obtained so-called troostite, martensite-troostite or martensite, all of which had a needlelike structure in contrast to the parallel plate structure of pearlite. In other words, at 1100° F. the type of transformation changed. Above this temperature we get parallel plates of material separating. Below this temperature we get needles, separating. As the temperature falls, these needles get more pronounced. At 400° F. they are very pronounced, and the authors call the structure martensite-troostite. At 150° F. it is pure martensite.

It seems to me that it is at 1100° F. that the change of method of transformation occurs, because it is here that you get the change in type of structure. If that is so, why do you get the acceleration of the transformation at 300° F. instead of just below 1100° F.? It is for that reason I do not think that the explanation given by the authors is the whole story, and I feel that if somebody could explain that change of structure, we would be a little nearer the required answer.

A. V. DEFOREST, Bridgeport, Conn.—I want to add emphatic words of praise for this paper because I know from experience how much it means to everybody who has worked in this field. It is the key that opens the door to an infinitely more accurate knowledge of what we are doing when we are heat-treating steel. I only hope that the authors will continue from this brilliant beginning and walk into the room that is now lighted up but still bare, and tell us something of the physical properties, in

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other words, the practical aspects that follow this illumination. From what glimpses we have had of the physical properties as interpreted in this light, it seems as though there would be an enormous advantage to be taken from some of the mechanisms involved in this delayed quenching affair.

Honda pointed out, I believe, that a delayed quench, in the sense of a slowly formed martensitic structure, had an enormously increased impact value compared with a martensite of exactly the same hardness which was formed more rapidly. In attempting to make use of that reaction, we have studied some of this type of quenching on wire. The practical man was quenching his wire in molten lead long before delayed transformation was even suspected.

H. Scott, East Pittsburgh, Pa. (written discussion).—The authors of this paper have had the rare privilege of examining structures in steel which are entirely novel as regards the method by which they are developed. They describe their microstructures in terms of the structural units normally found after continuous quenching or tempering after such quenching. This raises the question as to whether or not all their structures are equivalent to those obtained in the conventional manner. Unfortunately, the authors do not identify their photomicrographs in terms of the heat treatment represented nor give photomicrographs of samples quenched and tempered to the same hardness in the conventional manner, information which might assist in clearing up the question stated.

With further regard to the microstructural aspects of this paper, the authors are to be commended for making an effort to define clearly the major microconstituents of hardened steel. I refer in particular to their recognition of what may now be considered a fact; namely, that "nodular troostite" is actually pearlite in a very fine state of division. This restricts the use of the term troostite to the description of structures obtained only on tempering or perhaps to quenching as they have carried it out. Regarding the martensite decomposition structures, they are explicit only as far as visual features are concerned. This situation, however, cannot be avoided unless those microconstituents are defined ultimately in terms of the physical properties of the metal, as it is entirely feasible to do, but which has not as yet been attempted. Regarding sorbite, they are justified in omitting this constituent from their list, but hardly to omit this term for the description of a product of tempering. It would be interesting to know whether or not the authors intend to imply that.

The charts showing the time required for completion of the transformation of austenite into the end products noted are of great interest. The authors apparently have not been quite successful in orienting their findings with the previously known phenomena of quenching. That is not surprising, in view of the complexity of the reactions, nor is it likely to be achieved until more experimental data are available. It may help, however, to analyze their findings from a rather different viewpoint than theirs

When steel cools slowly at a constant rate from above the critical range, pearlite forms in a well understood manner. If the cooling is rapid and is suddenly interrupted, as in the authors' experiments at temperatures above about 500° C. in the case of steel B, the end product is the same and consequently the mechanism of its formation is the same as on slow cooling at a constant rate. The reaction occurring after interruption of rapid cooling at a low temperature, say under 100° C., is equally well understood though of quite a different nature. In this case the carbide is held in solid solution in the austenite matrix throughout the whole range of rapid cooling. Consequently the transformation Ar<sub>3</sub>, identified under these conditions by Ar", is lowered more or less in proportion to the amount of carbon in solid solution and in just the same way as it had been lowered by an equivalent amount of nickel or manga-

nese. The end product is martensite, which presumably contains as formed the same amount of carbon in solid solution as did the austenite from which it originated. Precipitation of carbide from the martensite starts and proceeds to the same degree as if formed near room temperatures and reheated for an equivalent temperature-time. Thus the phenomena occurring at either end of the temperature scale involved are simple at least in the sense that they are familiar.

Evidently there is a transition with diminishing holding temperature from the high-temperature or eutectic type of transformation, Ar', to the lower temperature or solid solution type, Ar". The nature of this transition is of great interest. Is it discontinuous, as when the rate of cooling alone is varied? Apparently it is, for the authors indicate a change in structure from the fine pearlite to troostite with a hardness difference of only one point Rockwell. Does this position on their chart, Fig. 7, between 550° and 600° C. represent the temperature at which the mechanism of transformation changes from the cutectic to the solid solution type or does it simply represent the limit of resolving power of their microscope? I doubt that this point can be definitely settled, however, without other physical tests than hardness, of which resistivity and density are particularly appropriate.

At holding temperatures below 400° C., the reactions are certainly of the solid solution type, but are somewhat more complicated than those occurring near atmospheric temperature. Nevertheless it is possible to give a simple description of what happens. Here after rapid cooling is stopped, precipitation of carbide from the austenite matrix starts and continues until the concentration of dissolved carbon in the matrix diminishes to the value at which Ar" starts at that temperature under continuous cooling. Afterwards the reaction goes on as stated for temperatures below 100° C., steel B.

According to this view of the phenomena, precipitation of carbide from austenite controls the start of Ar" in the temperature range 400° to 250° approximately. The lower the holding temperature in this range, the slower the rate of carbide precipitation and consequently the longer the time before Ar" starts. This corresponds with Fig. 5 of the paper, but is not the whole story because the degree of carbide precipitation necessary to start Ar" is smaller the lower the temperature. Of the two opposing factors, the rate of carbide precipitation is evidently the dominating one, because the time required for the start of Ar" increases with diminishing holding temperature.

The foregoing description of the reactions with time at constant quenching-bath temperatures no longer alone accounts for those observed when the bath temperatures are below the temperature at which Ar" starts during continuous quenching in a steel of given composition and quenching temperature. Then Ar" starts just as it does on continuous quenching, but from the expansion data of Fig. 5, it does not go to completion until a considerable time, during which no apparent reaction occurs, has elapsed. Thus there are two stages in the progress of Ar" in the temperature range 225° to 150° C. or thereabouts. The second stage is undoubtedly a continuation of the type of reaction observed at higher temperatures where precipitation of carbide from the austenite matrix is the controlling factor. One might expect these two reactions to go on concurrently and overlap so as to be indistinguishable. That they do not indicates that some factor other than those already considered is operating here to restrain Ar".

The missing factor is the same as that which controls the transformation of residual austenite on tempering high-carbon steels after a normal quench, a reaction that is essentially the same as that with which we are now concerned. This factor is, the writer believes, pressure created by the expansion accompanying Ar" after a continuous network of martensite is formed. The argument supporting this view is

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given in a previous paper.<sup>13</sup> If pressure is the controlling factor then tempering of the martensite network is the key that releases the pressure and allows Ar" to start again in the second stage. As the pressure development would also stop Ar" in the first stage of the reaction, we have an explanation of the two stages shown clearly by the authors' expansion curves.

Summarizing this discussion of rapid cooling arrested at temperatures ranging from the critical point to atmospheric, the products pearlite and martensite are formed in their respective ranges of holding temperatures just as on continuous cooling. Between these extremes is a temperature range in which carbide precipitation from the austenite matrix at constant temperature controls the start of Ar". The product of this change is troostite, which may or may not be identical in physical properties with that produced in the conventional way. There is a transition zone between this reaction and that producing martensite, in which both types occur in a manner entirely consistent with the normal reactions of tempering. The nature of the transition zone between the intermediate reaction and that producing pearlite is, however, not clear. These reactions may or may not overlap; the evidence available is insufficient to determine which is the case. Here also the factor that determines which type of reaction shall occur, that is Ar' or Ar", is not evident. It may be the rate of migration of carbon in austenite or again the temperature at which Ar" starts with minimum carbon in saturated solid solution. Any further information the authors may have which bears on these evasive points will be of great interest.

Finally, the authors' experimental technique is worthy of comment. Their expansion measurements are certainly open to the criticism that they are not precise, but to the writer's mind such criticism is academic. He has accepted their data as reasonably representative of what would be obtained under ideal conditions because they have shown a well-balanced sense of values in choosing their experimental conditions. Such experimental data might be properly classified as semiquantitative, and though less desirable than purely quantitative work, it is much to be preferred over the qualitative work in this field with which the literature has been so overburdened in the past. They are to be congratulated on the skilful execution of a well-conceived investigation.

S. L. Hoyt, Schenectady, N. Y. (written discussion).—Messrs. Davenport and Bain are to be congratulated on both the conception and execution of an extremely interesting research on the transformation of austenite. Much new information is offered and new means of correlating old data are made possible. In particular, the authors have dealt with the rates at which austenite transforms into ferrite plus cementite at high temperatures and into martensite at low temperatures. In so far as I know, this is the first time that has been attempted and adds much valuable information to the small amount available on reaction velocities in metallic systems. The authors might well attempt an analysis of their results in the light of previous work on chemical systems, if for no other purpose than to set up a simple example of such a reaction.

The information given in the paper is probably not complete enough to enable others to do this but we may at least draw the outlines of such a problem. Down to about 250° C. the steel B shows the characteristics of a system changing from a metastable to a stable system and by the process of nucleation and subsequent growth. The inverse curve of that given by the authors in Fig. 7, showing the time at which the transformation begins, would give the nuclei number curve. It is obvious that nucleation is controlling over this temperature range, and that the reaction products are ferrite and cementite. This transformation can be compared to the solidification of a cutectic, the chief difference being the relatively large degree of super-cooling

<sup>&</sup>lt;sup>13</sup> H. Scott: Dimensional Changes Accompanying the Phenomena of Tempering and Aging Tool Steels. Amer. Soc. for Steel Treat. (1926) 9, 277.

secured with austenite. While the authors give but few details of their method of determining the relative amounts of the phases present, it is to be presumed that their microscopical method gave correct estimates of the volume or weight percentages of austenite at different times and at the different temperatures.

The next simple reaction seems to be the one at or just above room temperature. Here the incubation period is absent and we may assume that nucleation does not control this transformation. It is not necessary for atoms of the new phase to arrange themselves in nuclei formation. Rather, a simple structural change occurs, possibly the einfache schiebung which was recently suggested by Scheil, which results in martensite or in a change into body-centered iron. Unfortunately for the purposes mentioned above, temperature has the reverse effect here as compared to its effect on chemical reactions, for the velocity of this change is shown to increase with decrease in temperature. At temperatures intermediate between these two, a more complex change occurs. The beginning of the transformation over the range from 160° to 250° C. for steel B is probably also due to the change to martensite, for this is sugg₃sted by both the structure observed with its martensitic markings and also by the times at which the transformations begin which fall on a smooth curve with those times for the temperatures below 160° C. Subsequent events greatly affect the course of the transformations and this may be nucleation in the martensite. This is suggested by the horizontal portions (incubation periods) of the curves for 160° and 180° C. in Fig. 5 followed by a rise later on.

A word of caution is called for by the use the authors make of length measurements as measurements of the amounts of the reacting phases. In metallic systems this particular point has always been a stumbling block to theoretical considerations. Over the higher temperatures the authors have arrived at a happy solution but I believe they should justify this use of length measurements over the lower ranges. Some time ago I attempted to make just that use of the shrinkage measurements of C. F. Brush which involved the change of martensite at room temperature, and the one positive point evolved was that the rate of change in length was not a measure of the reaction velocity. This was briefly dealt with in the Transactions of the American Society for Steel Treating, 14 while the whole paper in which this reference occurs deals with the anomalous relationships that exist between length and volume changes which militate against this use of length changes. I realize that the authors have taken the precaution of comparing the results of their two methods over intermediate temperatures but I do not believe that is sufficient. Aside from mentioning this point I do not wish to labor it, for with the objects of the present paper in mind, the authors would probably consider it of secondary importance.

I was interested in the authors' suggestion that negative pressures assist the formation of martensite. This must certainly be true when the conditions are correct, but it has been my understanding that the first martensite to form does so in spite of compressive stresses. During the quench the outer layers are under tension and the inside is under compression, at about the time martensite begins to form. This is because the outside is fairly rigid while the inside is shrinking. I believe that negative hydrostatic pressures account for deep hardening but that martensite forms on the outside in spite of compression, somewhat as outlined on pages 515 and 516 of the paper cited above.

G. M. Robertson, London, England (written discussion).—It has long been known that the essential factor in the hardening of steel is the maximum rate at which austenite can decompose in the range of temperature between 500° and 600° C.

<sup>&</sup>lt;sup>14</sup> S. L. Hoyt: Stresses in Quenched and Tempered Steel. *Trans.* Amer. Soc. for Steel Treat. (1927) **11**, 522.

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(930° to 1100° F). It is this maximum rate of decomposition that determines the critical rate of cooling necessary for hardening. Some very laborious investigations have been carried out in order to ascertain empirically the relations between mass, content of alloying elements, and rate of cooling, in determining hardening; but the present paper suggests a more conclusive and more scientific method of attaining this end. Alloying elements enable steel to be hardened with slower cooling and throughout larger masses because they reduce the maximum rate of decomposition of austenite. If, therefore, this maximum rate was determined for steels containing different amounts and different combinations of alloying elements, a quantitative estimate of the effect of these elements would be obtained. Each alloying element could then be given a factor expressing its relative effect on the maximum rate of decomposition, and this factor would represent the effect of the element on the rate of cooling required for hardening, and on the depth to which hardness would penetrate.

In one respect, the results obtained by the authors do not agree with existing data, and would be difficult to fit into any general theory of hardening that tried to account for certain other phenomena exhibited by steel. The results appear to show that at temperatures below 150° C. (300° F.), the decomposition of austenite proceeds with great rapidity at constant temperature, and the authors have accepted this as a fact. There is no doubt that the transition from austenite to martensite must be capable of taking place with great rapidity, for in unalloyed steels with less than 1 per cent. of carbon it cannot be appreciably prevented, even when the smallest specimens are cooled at the most rapid rates available. This only shows, however, that the transition takes place with great rapidity during continuous cooling, and does not necessarily imply that there is a range of temperature in which the austenite-martensite transition can take place with great rapidity at constant temperature. If, as the authors suggest, the austenite-martensite change was very rapid at constant temperatures below 150° C. (300° F.), then surely austenite retained by quenching would transform rapidly on tempering in this range. This, however, does not occur, and the tempering of austenite at low temperatures is actually very slow. To reconcile the facts of quenching with those of tempering, it is necessary to conclude that at temperatures below 300° C. (570° F.) there is a pronounced difference between continuous cooling and constant temperature. In support of this the following examples may be cited.

Matsushita<sup>15</sup> cooled specimens in water until the Ar" change began. He then withdrew them from the water and held them in air for varying times, and finally cooled them to ordinary temperature in water. He found that the decomposition of the austenite proceeded rapidly while the specimen was cooling in water, that it practically stopped when the specimen was held in air, and that it again proceeded rapidly when the specimen was replaced in the water. He further found that if the final cooling was performed in oil instead of water, the time required to complete the change was proportional to the rate of cooling.

Tammann and Scheil<sup>16</sup> observed a similar phenomenon when austenite retained at room temperature by quenching was cooled to lower temperatures. In other words, they found that the austenite decomposed as the temperature was lowered, and ceased to decompose when the temperature was held constant. In fact, when austenite is retained in association with martensite at ordinary temperature, it remains undecomposed because the temperature has ceased to fall, and because its decomposition is infi-

<sup>&</sup>lt;sup>15</sup> T. Matsushita: Some Investigation on the Quenching of Carbon Steels. Sci. Repts. Tohoku Imperial University [1], (1923–24) 12, 7.

<sup>&</sup>lt;sup>16</sup> G. Tammann and E. Scheil: Die Umwandlungen des Austenits und Martensits in gehärteten Stählen. Ztsch. f. anorg. Chem. (1926) 157-158, 1.

nitely slow at constant room temperature. When, however, the steel is cooled below ordinary temperature, the transformation proceeds rapidly as the temperature falls.

Andrew, Fisher and Robertson<sup>17</sup> have also shown that austenite decomposes rapidly during cooling and slowly at constant temperature, and similar conclusions may be drawn from the work of Lewis.<sup>18</sup>

All these results go to show that the decomposition of austenite at constant temperature is a function of time; the lower the temperature, the slower the decomposition. During continuous cooling, however, the decomposition is a function of the cooling; it proceeds as the temperature falls and at a rate that depends on the rate at which the temperature falls.

The temperature range in which austenite decomposes rapidly during continuous cooling is the range in which it can transform to a solid solution of carbon in  $\alpha$  iron; that is, the range below 300° C. (570° F.). If the austenite is quenched in any media held at a temperature below this range, the decomposition takes place before the temperature of the media is reached. The remarkable increase in the rate of decomposition of austenite observed by the authors at temperatures below 150° C. (300° F.) is therefore not attributable to an increase in the rate of decomposition at these temperatures, but to the fact that the change takes place during the few seconds required for the specimen to reach the temperature of the bath. When this temperature is attained, the change stops or proceeds very slowly at a rate that depends on the temperature. When the specimen is removed from the media, the decomposition again proceeds rapidly during cooling to room temperature. Acceptance of this view does not detract from the value of the results obtained by the authors, but it brings their results into line with existing data. The theory of the phenomena described has been outlined by Fisher and Robertson<sup>19</sup> and is fully described in my paper on The Effect of the Rate of Cooling on the Structure and Constitution of Steel.20

E. S. Davenport and E. C. Bain (written discussion).—We wish to express our thanks to all who so generously contributed to the discussion. Many have aptly elaborated our own ideas on some of the points treated only briefly in the printed paper, while others have made valuable suggestions for future work along these lines.

In the interest of brevity, we will attempt to answer most of the points raised in the discussion by presenting in some detail our own ideas of what takes place when steel is quenched. Any points that do not seem to have been covered in this manner will then be taken up separately.

Extending somewhat the views expressed in the paper we vision the mechanism of the transformation as follows:

Transformation in the Range from the Eutectoid Temperature Down to Ar'

In this temperature range the transformation proceeds by rhythmic, alternate rejection of carbide and ferrite from the austenite of approximate eutectoid composition. The time required varies from infinity at the cutectoid temperature down to a very short time in carbon steel at the Ar' zone, in strict accord with chemical reactions in general, in which a stable form is developed from a metastable one. Alloy steels

<sup>&</sup>lt;sup>17</sup> J. H. Andrew, M. S. Fisher and J. M. Robertson: Some Physical Properties of Steel and Their Determination. *Proc.* Royal Society (1926) A 110, 391.

<sup>&</sup>lt;sup>18</sup> D. Lewis: The Transformation of Austenite into Martensite in a 0.8 Per Cent. Carbon Steel. *Jnl.* Iron and Steel Inst. (1929) **119**, 427.

<sup>&</sup>lt;sup>19</sup> M. S. Fisher and J. M. Robertson: Discussion on (4).

<sup>&</sup>lt;sup>20</sup> J. M. Robertson: Great Britain Scientific & Industrial Research Dept. Safety in Mines Research Board Paper 61. H. M. Stationery Office, London, 1930.

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are hardenable by water quench, oil quench or air cooling, depending wholly upon the time required for transformation at the temperature of most rapid action; i.e., Ar'. The product of transformation at these temperatures is pearlite of a coarseness depending upon temperature; the pearlite later spheroidizes if maintained at constant temperature. The transformation in this range of highest temperatures is comparatively simple.

## TRANSFORMATION IN THE RANGE FROM AR' DOWN TO ABOUT AR"

In this temperature range the transformation time increases steadily with reduction of temperature of transformation, which is also in accord with the generally observed speeds of chemical reaction in the cases wherein atomic mobility plays an important role, superimposed upon the effect of remoteness of temperature from that of equilibrium between the two phases involved. The product of transformation in this range is distinctly different from that in the higher temperature range described The lamellar type of ferrite-cementite association does not appear to exist; instead there is reason to believe that the austenite transforms at least momentarily to ferrite, from which the carbide then immediately tends to precipitate. The reason for this surmise is that acicular markings, faint in the highest temperature products within the range and most distinct in the lower temperatures, are always microscopically visible. Probably the carbide rejection is almost simultaneous with the allotropic change at the elevated temperatures, but may lag far behind at the lowest temperatures in this range. The intermediate cases in the temperatures between those forming typical fine nodular pearlite and those forming recognizable, acicular troostite are very interesting and substantiate this view, for one frequently observes both types of structure associated in the same specimen. We infer that the nature of the structure is due wholly to relative rates of allotropic transformation (einfache schiebung referred to by Dr. Hoyt) and carbon migration or diffusion, and not directly dependant upon the time per se. This brief outline of the explanation most acceptable to us, at least at the present, relates particularly to the very apt criticism of Mr. Lewis, whose suggestions have been most valuable to us in reviewing our observations.

We would especially commend the use of Mr. Scott's terms "eutectic or Ar' type" of transformation and the "solid solution or Ar" type" for what we have spoken of as "pearlitic" and "acicular" type. In this discussion we have continued our nomenclature only to avoid confusion, but the foregoing paragraphs are intended to reply to a portion of Mr. Scott's most important discussion. Our own present opinion, admittedly not necessarily our final one, does not favor his suggestion that carbide precipitates first from the austenite, although a low-carbon austenite would inaugurate Ar' at a higher temperature than an austenite of full eutectoid carbon content, a indicated in the charts of low-carbon steels.

#### TRANSFORMATION AT AR"

The transformation of austenite at these low temperatures appears to be practically instantaneous. Carbide precipitation is almost perfectly inhibited and the martensite seems to form by the propagation of an eruptive wave through the austenite grains. This wave, if the expression may be permitted, is merely the slight shifting of atoms in the 111 atomic plane of austenite to form the 110 plane of less perfectly crystallized ferrite with carbon still atomically dispersed in a concentration far in excess of saturation. So far as our speculation has gone, there is no very clear explanation for the extraordinary circumstance of a transformation proceeding in a most leisurely fashion at about 300° F. (150° C.) suddenly completing itself in a few seconds at a temperature only 100° F. (55° C.) lower! We are therefore especially grateful for the explanation offered by Dr. Robertson and for the suggestion of Mr. Lewis, which shed light upon

this phase of the problem. In the absence of more satisfactory explanations we have mentioned the "negative ferrostatic pressure" but certainly do not feel justified in defending that idea very vigorously. The only objection we have to the Robertson theory of the transformation requiring a falling temperature for its procedure is found in our specimens which had appeared to reach a zero rate of change after a few minutes at a constant temperature of about 285° F. (140° C.). No further transformation, as evidenced by expansion data, was observed when such specimens were subsequently cooled to 70° F. (20° C.). Evidently the transformation had completed itself at constant temperature in a few minutes at 285° F. (140° C.) since no austenite remained to transform upon further rapid cooling.

Referring now to some other specific points brought out in the discussion. We would not wish to be misunderstood as suggesting any significant changes in nomenclature. Indeed, we have only omitted the word "sorbite" in discussing the structures found in our various series for the reasons indicated, and certainly have no doubts at all as to its having the most definite sort of meaning as applied to tempered structures. Possibly some of the structures designated as troostite, if retained at the bath temperature for extended periods of time, would have changed by carbide coalescence to a product to which the name "sorbite" would apply appropriately.

The microstructures of similarly treated specimens from the various steels investigated resemble one another sufficiently to warrant the expedient of printing only representative photomicrographs. Figs. 15 to 20 inclusive are of steel A; Figs. 15 and 16 are from the 1275° F. (691° C.) bath temperature; Figs. 17 and 18 are from the 1200° F. (694° C.) bath temperature; Figs. 19 and 20 are from the 800° F. (427° C.) temperature. Figs. 21 and 22 are of steel F as transformed respectively at 284° F. (140° C.) and at 527° F. (275° C.).

At the present time we are engaged in establishing the fundamental difference between steels transformed at elevated temperatures and steels which first transformed to martensite and subsequently were tempered, or drawn back, to comparable physical properties. In our experience the microscopic appearance is quite different when corresponding temperatures are employed.

The expansion measurements employed to follow the progress of the reaction are unquestionably not adequate, as pointed out by Dr. Hoyt. We are of the opinion, however, that the end of the transformation is fairly well marked by the end of the expansion period. Accordingly we have not drawn any conclusions involving the rates of reaction in the lower temperature ranges.