THE ISOTHERMAL DECOMPOSITION OF AUSTENITE
IN THE BAINITE REGION

by

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ABSTRACT

The isothermal decomposition of austenite in the bainite region has been examined. The progress of the transformation in several hypoeutectoid and eutectoid steels was investigated metallographically from a qualitative point of view. A survey was made of the information available on the initiation, course, and end product of the transformation.

The factors entering into the transformation were examined separately, their temperature-dependence and interactions investigated. A theory of the decomposition of austenite was proposed, and this theory examined in the light of the phenomena associated with the isothermal and anisothermal progress of the transformation.
INDEX

I INTRODUCTION .................................................. 1

II EXPERIMENTAL METHODS ........................................ 3

III DISCUSSION

(a) The Isothermal Transformation of Austenite in the Bainite Region ............................................. 5
(b) The Shear Mechanism of Bainite Formation .................. 12
(c) Lattice Coherency .................................................. 12
(d) The Effects of Residual Stresses ................................. 14
(e) Behaviour of the Carbon .......................................... 15
(f) The Extension of Ferrite Regions Without Shear .......... 17
(g) The Energy Change in Bainite Formation ..................... 19
(h) Nucleation .......................................................... 20
(i) Growth ............................................................... 22
(j) The Process of Reaction in the Upper Temperature Region .................................................... 24
(k) The Process of Reaction in the Lower Temperature Region .......................................................... 25
(l) Effect of Grain Size .................................................. 26
(m) Anisothermal Behaviour ............................................. 27

IV SUMMARY ............................................................. 32

V ACKNOWLEDGEMENTS ............................................... 36

VI BIBLIOGRAPHY ........................................................... 37
THE ISOTHERMAL DECOMPOSITION OF AUSTENITE
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I - INTRODUCTION

Although there has been a great deal of information published on the theory of the decomposition of austenite in the bainite region, and many theories have been advanced to explain different phenomena associated with this decomposition, there has been no recent summary of the available knowledge in this field. The object of the present investigation is to bring together and correlate the existing data, with a view to assisting in providing a better understanding of the mechanism of the reaction.

The nature of the transformation of austenite in the bainite region renders its study particularly difficult. Two interdependent mechanisms of transformation are available; (a) precipitation and growth by diffusion, and (b) phase change by martensitic shear. Since both are temperature-dependent, the complications of the transformation are reduced if the process is carried out isothermally rather than during continuous cooling. As some of the factors involved, such as variation in carbon concentration on a micro scale, and
distribution of internal stress, may not be directly observed, their importance must be deduced from the observable phenomena and results associated with the reactions occurring during transformation and other reactions of a similar nature. This restriction prevents the quantitative evaluation of the rate and course of the transformation from basic principles but, from a knowledge of the reaction behaviour at different temperatures of transformation, the relative importance of the different factors may be estimated.

In this investigation the different reactions have been examined individually from a thermodynamic and kinetic viewpoint. Their variation with temperature has been indicated. The interaction between the individual reactions has been investigated and a theory proposed for the decomposition process. This theory has been applied to the experimental data available.

Where the terms bainite and ferrite are used in many places interchangeably throughout this report, bainite generally is taken to refer to the labile aggregate of carbide plus ferrite (possibly supersaturated with carbom), and ferrite to refer to the body-centered cubic form of iron, whether supersaturated with carbon or not, and whether formed by shear or by a diffusive growth.
II - EXPERIMENTAL METHODS

The structures of a number of low-alloy hypo-eutectoid and eutectoid steels have been examined microscopically after having been partially transformed isothermally at various temperatures in the bainite region.

The initial stages of isothermal transformation have been investigated in a series of steels with 0.55% Carbon, with and without 0.35% Molybdenum and with varying Nickel content. The preparation of these alloys has been described elsewhere\(^1\). A similar series with higher carbon analysis (up to 0.80 weight percent) was investigated in the region of bainite formation. Various low-alloy commercial steels have been examined to varying extents.

The specimens were prepared as flat discs approximately 0.05 inches thick. A wire was attached to each to facilitate handling during heat treatment. The specimens were austenitized for 15 minutes at 1600° F. in a neutral salt bath, quenched to, and held for a measured time at, the isothermal transformation temperature in a salt bath, and immediately brine-quenched to room temperature. The treated specimens were ground on emery to remove any possible surface effects and to prepare for polishing. The specimens were polished electrolytically using a mixture of perchloric and acetic acids, 185 ml. perchloric acid, specific gravity 1.61 gm./c.c., 165 ml. acetic acid, 10 ml. water, with some aluminum introduced into the solution\(^2\). The principal
The etchant used was 2% nital containing 1% Zephiran Chloride. This preparation of the specimen to be examined was found to produce a highly-detailed undisturbed surface.

Structures shown in the accompanying micrographs were obtained by treating commercial SAE 1080 steel containing 0.75% Carbon. The micrographs were taken using an oil-immersion objective of N.A. 1.32.

In interpreting these micrographs it should be noted that the magnifications are sufficiently large that the observed structure in the field shown may not be truly representative of the degree of transformation throughout the specimen.

In the following discussion, the results of this metallographic investigation are given together with a survey of the published results of other investigations. Leading references have been given for results drawn from the literature. In some cases references have been cited for evidence supporting the results of this investigation.

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* 8% aqueous solution, distributed by Winthrop Chemical Company, Inc., New York, N.Y.
III - DISCUSSION

(a) The Isothermal Transformation of Austenite in the Bainite Region.

In the early stages of formation, bainite occurs as lamellae nucleated on the grain boundaries (Fig. I). These lamellae consist of ferrite, possibly supersaturated with carbon at lower temperatures, and carbide particles, precipitated on the ferrite-austenite interface in the early stages. Evidence has been given that the habit plane of the bainite in relation to the parent austenite changes with temperature of transformation, and that the orientation of the ferrite in bainite is independent of temperature of formation, being the same as proeutectoid ferrite. The cementite is in a fine state of dispersion, X-ray line intensities being considered comparable with those of tempered martensite. The results of magneto-metric investigations have been interpreted to indicate that in alloy steels, the carbides tend to be closer to the simpler Fe₃C composition as the temperature of transformation is lower.

During transformation in the upper temperature regions the lamellae when initially formed are irregular, often occurring in groups of lamellae with similar orientation (Fig. I). These lamellae grow as blocky formations (Fig. II) or, sometimes, in lens shapes which are more concave at higher temperatures (Fig. III). Nucleation apparently stops soon after the initial period, and the lamellae agglomerate by side-growth. The
transformation at high temperatures goes to completion by the agglomeration of existing plates followed by the extension of regions so formed, resulting in an aggregate of ferrite and cementite. Bainite formed in the lower temperature range is finer in structure, less irregular in cross-section, and more uniform (Fig. IV). As the temperature of transformation is lowered the tendency of the lamellae of the same orientation to group together becomes less apparent\(^5\) (Fig. IV). The decomposition of the austenite in the lower range goes to completion by the formation of new lamellae, apparently nucleated by existing plates.

Analysis of the over-all transformation rates\(^7\) has shown a progress from three-dimensional towards two-dimensional growth as the temperature of isothermal transformation is lowered.

There is evidence\(^5,^8\) that carbon enrichment of the untransformed austenite occurs with the formation of bainite. This has been shown to be thermodynamically likely\(^9\). The enrichment of the austenite by carbon from the bainite is countered by carbon depletion during carbide formation\(^10\).
Figure I

SAE 1080, partially transformed isothermally at 700° F.  
2000x.  
Electropolished.  
Etched in 2% nital with Zephiran Chloride.

The two micrographs above show the appearance of the initial high-temperature bainite formation. The bainite is in groups of irregular similarly-oriented lamellae. The grain-boundary origin of the bainite may likewise be observed.
Figure II

SAE 1080, partially transformed isothermally at 800° F.
2000 x. Electropolished.
Etched in 2% nital with Zephiran Chloride.

This micrograph shows an extreme form of high-temperature bainite. The growth is acicular, but the rate of agglomeration of the lamellae by sidewise growth is rapid, therefore only the advancing edges of the plates in a group are separate.

This specimen was cooled to the isothermal transformation temperature slowly enough to permit the formation of some nodular pearlite.
Figure III

SAE 1080, partially transformed isothermally at 600° F. 2000 x. 
Electropolished. 
Etched in 2% nital with Zephiran Chloride.

These micrographs illustrate the intermediate-temperature bainite growth. Parallel lamellae occur in groups in the early stages. The lamellae thicken as they grow, often becoming lens-shaped as illustrated. Few new bainite plates appear in the later stages of growth, the transformation going to completion by agglomeration.
SAE 1080, partially transformed isothermally at (a) 450° F., and (b) 500° F.
2000 x. Electropolished.
Etched in 2% nital with Zephiran Chloride.

Low-temperature bainite is finer and more regular than that formed at higher temperatures. The tendency for parallel lamellae to occur in groups is less, as is here shown.

New plates are formed throughout the course of the reaction.
SAE 1080, partially transformed isothermally at 700° F.  
2000 x.  
Electropolished.  
Etched in 2% nital with  
Zephiran Chloride.

The above structure follows a grain boundary. The irregular agglomerated structure with associated lamellae is typical of the high-temperature reaction in the early stages of growth.
(b) **The Shear Mechanism of Bainite Formation.**

From crystallographic and structural considerations, bainite is generally considered to be formed, in the early stages at least, by a lattice shearing process, comparable to martensite formation. Such a mechanism is to be expected at temperatures where the self-diffusion rate of the iron is low; the shear process requires only a small movement of atoms from the positions in the parent phase to the positions in the new phase, and hence will take place easily\(^{11}\). The formation of bainite takes place as a time-dependent growth process, as opposed to martensite formation, which, disregarding relaxation effects, is essentially independent of time. Martensite formation in this respect, resembles mechanical twinning\(^{12}\). Since bainite formation is a shear-type reaction, it will produce residual shear stresses. Also, since the specific volume of bainite is greater than that of austenite, shear stresses are set up by the formation of bainite because of this increase in volume. The relationship of bainite to the parent austenite is such that coherency of the lattices at the interfaces may exist if the bainite is compressed and/or the austenite stretched within limits outlined in the subsequent discussion.

(c) **Lattice Coherency.**

The problem of forced lattice coherency has been investigated in the case of precipitation of lamellar structures from solid solution\(^{13}\). The reasoning and results may be applied to bainite formation to yield a rough estimate of the
maximum size of bainite which may be coherent with the parent austenite. The plate thickness increases until the strain energy is equal to that required for the formation of a disordered interface. This thickness is of the order of $100/d$ atom diameters, where $d$ is the percentage misfit between the two lattices on the interface plane. In addition to the assumptions used in reference 13), (namely: that the material is isotropic; that all the strain is taken up in the precipitate; that the elastic equations of a continuous medium may be applied; that Hooke's Law will hold over the large strains involved), we have neglected in our application the effect of the shear stresses associated with bainite formation and the effect, probably not small, of carbon in solution in the bainite. This estimate is sufficient to indicate, however, that coherency will be probable only in those regions wherein the austenite strain is less restricted, as at the grain boundaries, and near the advancing edge of a bainite plate. We may expect the advancing edge itself to be coherent with the austenite, since the movement of an atom from its position in the austenite to its position in the bainite is small enough (approximately $1/3$ of the interatomic distance) that
local distortion will take up the discontinuity without breaking coherency.

A graphical representation of the strains produced near the growing edge of a bainite plate because of lattice coherency is given in Figure VI.

(d) The Effects of Residual Stresses.

Assuming a bainite plate to have formed, the shear stresses thereby produced will oppose a similar shear reaction with the same orientation, and assist shear reactions in other specified complementary directions. Considering Figure VII, if the bainite arises from a shear in the direction of the dotted arrows, it will produce shear stresses in the matrix as shown by the full arrows. Since the shear may occur in one direction only, the residual stresses act so as to oppose any bainite formation of similar orientation. There are, however, in any crystal of austenite several planes and directions along which the bainite formation may take place, and therefore the shear stresses may assist the formation of bainite along a different direction. The formation of bainite of such a comple-
mentary orientation would serve as a means of relaxation for the stresses set up by the first plate. Also, the stresses produced by a foreign particle or phase in a matrix are strongest near the particle, as may be deduced from the phenomenon of stress-relief by agglomeration in alloys having a highly-dispersed precipitate. The fact that parallel plates do not form so readily at lower temperatures can be accounted for by this process of reasoning.

(e) **Behaviour of the Carbon.**

It is considered that during the formation of bainite whole groups of atoms may move simultaneously from the old to the new phase, entrapping the carbon atoms\(^9\). This method of growth is to be expected, where possible, since the growth rate is faster and the activation energy is lower than for an ordered individual diffusion\(^{15}\). It does not, however, exclude the advancement of the bainite by a process of growth wherein the carbon is not trapped, but diffuses away or precipitates as carbide.

Any carbon atoms entrapped in bainite will have a higher rate of diffusion in the bainite than in the austenite. Taking activation energies of 18,000 cal/mol for carbon in ferrite\(^{16}\), and 32,000 cal/mol for carbon in austenite\(^{17}\), and the average time between basic acts of diffusion as being given approximately by

\[
t = \frac{hN e^H}{H/RT}
\]

- \(h\) - Planck's constant
- \(N\) - Avogadro's number
- \(R\) - gas constant
- \(T\) - temperature
- \(H\) - activation energy for a diffusion movement
we may calculate that at a temperature of 400° C. a carbon atom in ferrite is likely to have about 10,000 times as many changes of position in any given time as a carbon atom in austenite. This unbalance of diffusion rates, coupled with the large free energy change of carbon between austenite and ferrite will result in a rapid increase in carbon concentration in the austenite adjacent to a newly-formed block of bainite. There is considerable strain in the lattice near the interface, and if the bainite has lost coherency with the austenite we may expect a high mobility of diffusing atoms at the interface. The heat of reaction will assist a higher local mobility. Such conditions promote rapid nucleation of carbide, and hence will tend to precipitate the carbide in a very fine form. The fine size of the carbide will result in it having a lower alloy content than the equilibrium conditions at that temperature require, as has been observed and fully discussed. That the carbide of the simple Fe₃C structure should precipitate in preference to a more complex alloy carbide may also be deduced from consideration of the relative probabilities of forming critical size nuclei of the alternative carbides.

The problem of carbide precipitation is rendered more complex by the inequalities of concentration, that is, if by diffusion from a region of rapidly formed bainite, a high-carbon region is formed, under the conditions of rapid nucleation outlined above most of the nuclei will be of critical or near-critical size for that concentration of carbon. The concentration of carbon in the region where the carbides are precipitated is
reduced by diffusion towards the unreacted austenite, which is of lower carbon content, and by precipitation onto the carbides. Now, as the carbon concentration is reduced, the critical size of the carbide nucleus, below which the nucleus is unstable, increases. At temperatures of rapid diffusion, it is quite conceivable that the critical size of nucleus could increase at a greater rate than the increase in size by growth of the carbide particles present, and so could exceed the size of many of these, rendering them unstable. The unstable carbides would then redissolve. The result would be an increased carbon concentration in the unreacted austenite.

The carbide particles remaining after the carbon concentration has become more uniform continue to grow in a normal fashion. The growth of carbides implies a reduction in the carbon concentration of the surrounding austenite. This process acts simultaneously with the carbon-enrichment by bainite formation. At any one temperature of reaction, whether or not the unreacted austenite is enriched or depleted with regard to carbon will depend upon the relative rates of the bainite and the carbide reactions. One may expect that carbon-enrichment will occur when the bainite reaction is more rapid, depletion when slower. This is indicated experimentally\(^8,10\).

(f) **The Extension of Ferrite Regions Without Shear.**

If an austenite-ferrite interface is considered after it has lost coherency, it may be seen that individual iron atoms could jump from positions in the austenite to more stable positions
in the ferrite without increasing the shear stresses associated with the shear mechanism of bainite formation. Such a method of phase growth has been shown to be dependent upon the diffusion rate of carbon away from the interface\textsuperscript{9}). As a result of the concentration gradient caused by bainite formation, diffusion may increase the carbon concentration in the unreacted austenite. The amount of the enrichment will be influenced by the degree of carbide precipitation. Therefore three factors will largely control the rate of transformation of austenite to ferrite in this manner: the carbon concentration in the austenite remote from the interface, the activation energy of iron transferring across the interface, and the diffusion rate of carbon. The carbon concentration is dependent upon the degree of transformation, increasing in the upper bainite range, showing little change at lower temperatures. The temperature-dependence of the rate of growth attributable to the iron and carbon activation requirements will be of the form $\exp(-A/RT)$, where $A$ is proportional to the activation energies. Since the carbon diffusion rate is the predominant factor in such a reaction\textsuperscript{9}), the rate of growth will decrease approximately exponentially with temperature.

Growth in this manner will facilitate the segregation of any alloying elements, those such as nickel and manganese which have lower free energy when dissolved in austenite tending to diffuse away from the boundary so as to stay in the austenite, and those elements such as chromium which have lower free energy when dissolved in ferrite tending to enter the bainite. Such segregation has been advanced as an explanation for the abnormally
long times for completion of transformation in the upper bainite region in certain alloy steels\textsuperscript{5}).

\textbf{(g) The Energy Change in Bainite Formation.}

A phase change is possible only if the free energy is decreased by the reaction. Considering bainite formed by shear, with entrapped carbon, four factors determine the free energy change: the free energy change of the iron in going from the face-centered structure to the body-centered, $dG_{Fe}$; the difference in free energy between carbon in a face-centered cubic lattice, and carbon in the body-centered cubic lattice $dG_{C}$; the change in entropy of the carbon, $dS$; and the change in strain energy associated with the transformation, $dU$. This may be written as\textsuperscript{9}:

$$dG = dG_{Fe} + CdG_{C} - CTdS + dU$$

\begin{itemize}
  \item $C$ - carbon concentration
  \item $T$ - temperature
\end{itemize}

There is no need to consider surface energy if the lattices are assumed coherent at the time of transformation.

In any transformation there is a certain activation energy which controls the rate of reaction. For martensitic-shear reactions with small movements this is insignificant, however, and may be neglected.

Thus assuming that the transformation will occur whenever the free energy change is negative, we will examine the factors involved to account for the time-dependence of the bainite reaction.

$dG_{Fe}$, $dG_{C}$, and $dS$ are independent of time, but $C$, the carbon concentration, and $dU$, the strain energy change, will
fluctuate with time and with the degree of transformation. The carbon concentration will fluctuate by chance diffusion, by the effect of nearby bainite formation, by precipitation of carbides as described, and by variations in internal stress conditions. References 18, 20, 21). The internal stress will be very high under the initial effect of quenching, and will be raised by bainite transformation. It will relax at an appreciable rate in the temperature range of bainite formation. The relaxation rate is temperature dependent exponentially, of the form \( \exp(-B/T) \), where \( B \) is dependent upon the amount of internal stress.

If we consider a single bainite plate growing edgewise by shear, we may see that the rate will be restricted by the relaxation rate of the opposing residual stresses. As the temperature of transformation is lowered the decrease in free energy by the change of iron from the face-centered cubic to the body-centred cubic form increases rapidly, partially offsetting the decrease in the relaxation rate of the inhibiting stresses.

(h) **Nucleation.**

Metallographic examination has shown that bainite tends to nucleate preferentially on the grain boundaries\(^3,22\). This is supported by the examination of proeutectoid ferrite, which has a closely-related mode of formation, and which, because of its lesser tendency towards lamellar growth, shows more clearly its region of nucleation. There is evidence that nucleation and growth of bainite are greatly assisted by plastic flow\(^23\). Nucleation of bainite in the grain boundaries is to be expected.
The contribution to the strain energy by volume change is smaller at the grain boundaries\textsuperscript{13}. Amongst the disordered material there is a higher probability of finding sites particularly suited to nucleation\textsuperscript{24}. Regions having a favourable internal stress for nucleation may be expected because of the constraining effect of the grain boundaries, the variation in internal stress being particularly great during the time when quenching stresses are operative. Conditions of plastic flow produce both a large number of nucleation sites and a wide variation in internal stress. Better defined evidence of the effect of stress conditions is found in the case of transformation below the $M_g$ line\textsuperscript{25}. Here, bainite nucleates on the martensite needles, the transformation proceeding more quickly adjacent to the martensite than in the untransformed matrix. From this evidence it would be expected that grain size would greatly affect the number of sites of possible nucleation. In general, the probability that a preferred site of nucleation will transform into a nucleus is dependent in some manner upon the degree of transformation in the surrounding material\textsuperscript{24}. In the bainite transformation the probability is affected by three factors. Firstly, when the steel is quenched to the transformation temperature the stresses produced by the quenching will promote nucleation where they are, by chance, so oriented as to assist the bainite shear on any plane under consideration. This factor will be effective only at the beginning of transformation. Secondly, any increase in carbon concentration caused by previous bainite formation will inhibit nucleation. This factor will be
of greater importance at higher temperatures, and will be dependent upon the amount of bainite and precipitated carbide near to the nucleation site. Thirdly, stresses set up by the previous formation of bainite will inhibit nucleation of bainite of a similar orientation, as described, but may assist nucleation of bainite of a complementary orientation\textsuperscript{14,26}). The effect of this last factor will increase with the amount of transformation. It will have its greatest effect in the same regions, those near to previously formed lamellae, in which the carbon-enrichment factor will be strongest, but since stress relaxation decreases with temperature, the stress factor will increase with decreasing temperature. From these considerations it may be seen that the rate of formation of nuclei will be very high initially, but will decrease rapidly, the rate of decrease being less at lower temperatures. Further, the rate of nucleation will be affected by a change in the number of sites of possible nucleation, as by a change in the amount of grain boundary material. Direct observation of nucleation rates of bainite is not practical, but it is to be noted that at higher temperatures the reaction tends to go to completion by agglomeration, whereas at lower temperatures it progresses by the formation of new lamellae throughout the reaction period.

(1) \textbf{Growth.}

The isothermal transformation of austenite in the bainite region must be considered to take place by two different processes, one martensitic in nature, the other diffusive. The
former is strongly affected by the rate of stress relaxation, and both are affected by the behaviour of the carbon.

The martensitic-type reaction is nucleated on the grain boundaries. During growth it creates high residual stresses which inhibit the growth of similarly-oriented lamellae, and promote growth along certain other planes. The edgewise rate of growth is high, favouring continued extension in the same plane. The stress conditions may be expected to be analogous to those set up by martensite formation, and it may thus be assumed that the rate of transformation through shear is in this way controlled by the rate of stress relaxation. A relationship has been suggested between the induction period of bainite and the creep strength of the austenite. The formation of bainite causes rapid carbon precipitation and if the temperature is in the upper range raises the carbon concentration of the unreacted austenite. This increase in carbon inhibits the transformation.

The diffusion reaction may be considered as the addition of single atoms of iron to a nucleus of ferrite across a disrupted interface. The rate of a reaction dependent upon diffusion has been shown to decrease exponentially with temperature. At any one temperature of reaction the rate of transformation of austenite by this process will depend upon the area of ferrite-austenite interface. The flat plates formed by the shear reaction provide a large interface area, and so it is evident that the amount of transformation by diffusion increases rapidly as the amount of sheared product increases.
(j) **The Process of Reaction in the Upper Temperature Region.**

At higher temperatures the rate of diffusion and the rate of stress relaxation are greater. The change in free energy of the iron in going from the austenite to the ferrite is less, and carbon enrichment of the unreacted austenite is more likely. After the initial quenching stresses have relaxed the variation in stress conditions in the material will be very limited, since relaxation is rapid. For this reason sheared bainite is initiated upon quenching which, since the stress conditions promoting nucleation will often prevail over distances of a size comparable to grain radii, will tend to form in groups of parallel lamellae. Any plate within such a group will not inhibit independent growth of adjacent plates by reason of residual stresses, except when very close together, because of the rapid relaxation rate. As indicated under Nucleation, page 20, the number of nuclei formed after the initial stages will be very limited. The plates will extend edgewise by a continued shear action and sidewise by a diffusion reaction. The edgewise growth will stop at such discontinuities as grain boundaries, Figure I. The amount of austenite transformed by sidewise growth increases as the austenite-ferrite interface area increases by the shear reaction, and decreases as the interface area is decreased by the decrease of unreacted austenite. The rate of growth sidewise decreases as the carbon content of the austenite is increased by reaction (5). The type of growth curve indicated by this process is in accordance with those observed7).
The Process of Reaction in the Lower Temperature Region.

At lower temperatures diffusion and relaxation rates are lower. The free energy change of the iron transformation is greater, and less carbon enrichment of the austenite is likely. Because of increased free energy change the shear reaction is more likely to occur, and larger blocks of atoms may be expected to transform at one time, resulting in greater entrapment of carbon. The stresses set up will be larger as the temperature is lower since the relaxation rate is lower, and there higher stresses will inhibit nearby growth of a similar orientation, thereby both reducing the tendency to form groups of similar lamellae, and assisting growth of a complementary nature, which acts to relieve the stress, resulting in a criss-cross pattern. Sidewise growth is limited; the thermal energy being lower, the diffusion reaction will be inhibited by its activation energy. Sidewise growth by shear is inhibited by the contrary residual stress. The edgewise growth is such as to tend to keep the plates flat. The growth rate curve will be of a two-dimensional nature, as has been experimentally indicated.

This theory of growth explains satisfactorily the structures observed metallographically during the isothermal transformation of austenite: in the upper temperature range irregular coarse bainite, showing groups of parallel lamellae (Figs. I, III) tending to thicken as they grow, transforming only partially by formation of plates, and completing transformation by a thickening, diffusive process; as the temperature of transformation is lowered the bainite becomes more regular, fine, similarly-oriend...
-ted lamellae are less likely to occur in groups (Fig. IV), reaction proceeding to completion by the continued formation of new plates.

(1) **Effect of Grain Size.**

The effect of grain-size variance on the behaviour of the transformation\(^{22,28}\) is in agreement with the proposed theory of decomposition. Grain size in the lower range has no appreciable effect, in the upper range has very little effect on the initial stages of transformation but tends to accelerate the later stages of transformation. The lamellar structure of bainite is better defined when formed in austenite of large grain size\(^{28}\). The number of nuclei which grow will be determined by the stress conditions set up by their growth, not by the number of possible sites of nucleation. Therefore, although more sites may be activated during the initial stage before the quenching stresses have been relaxed, many of these will become inoperative because of the growth of nearby plates, and the growth rate of all plates will be reduced if the density of lamellae is greater. The overall transformation by shear will also be retarded by the constraining action of the grain boundaries\(^{29}\). Some more noticeable acceleration of the transformation occurs towards the upper temperatures\(^{28}\). The 1% transformation time is not appreciably altered, since the products appearing up to that stage are nearly all sheared, but that for 99% transformation is reduced, since the sheared products are spread out over more grain boundary area, and hence give a greater austenite-ferrite interface area,
allowing more rapid transformation by the diffusion mechanism.

(m) Anisothermal Behaviour.

Much useful information may be gained from a study of the effect of partial transformation at one temperature on the transformation at a different temperature level\(^{22,30,31}\). Partial transformation to ferrite (less than 1%) accelerates beyond additivity\(^{3}\)-subsequent bainite formation (1\%). It is indicated that holding a fixed time in the ferrite range accelerates formation of bainite by a percentage which is independent of the temperature at which the bainite forms\(^{30}\).

Considering temperatures above and below the nose of the ferrite "C" curve when the ferrite transformation is distinct from the bainite transformation, holding at a higher temperature in the ferrite region has a greater effect than holding at a lower temperature for which the time for 1% transformation is the same. An explanation of this has been put forth\(^{30}\) in terms of nucleation. Because, as has been shown, the transformation to bainite is less controlled by the number of nuclei than by the stress conditions, it is felt that this evidence should be discussed with regard to carbon behaviour and stress conditions. The proeutectoid ferrite reaction may be considered as an extended bainite reaction in which the carbon migrates away from

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\(^{3}\)A reaction is considered additive for a given amount of transformation if that amount of transformation occurs when the total fractional time integrated over the various temperatures of the reaction is equal to one, where the fractional time at a temperature is defined as the actual time at the temperature divided by the time necessary at that temperature to produce the given amount of transformation.
the ferrite into the austenite. Because of the relationship of the ferrite to the austenite some stress will arise from volume expansion and possibly from shear formation of ferrite. Consider a fraction of 1% transformation at three temperatures, two in the ferrite region, at a higher and lower temperature where the time for 1% transformation is the same, and one in the bainite region. The structures will be comparable in that they consist of ferrite having a similarly-determined orientation with regard to the parent austenite. The bainite will have associated with it residual stresses, some entrapped carbon and a carbon-enriched region surrounding it containing precipitated carbides. The ferrite will have associated residual stresses, much smaller, and less at the higher temperature, few precipitated carbides, and a carbon concentration in the surrounding austenite much less above that of the remainder of the matrix, since diffusion rates are higher in the ferrite range. When the ferrite is produced at the upper temperature there will be least localized increase in carbon. From this it may be seen that if austenite, partially transformed to ferrite is quenched into the bainite range we may consider the ferrite as bainite, without the high associated stresses and local increase in carbon concentration, and hence the reaction will go to 1% in a time less than that required by isothermal transformation at the bainite temperature alone.

Partial bainite formation (less than 1%) accelerates subsequent ferrite formation (1%) but the effect is less than that corresponding to additivity\textsuperscript{30}. This is explained in the
preceding paragraph, since the stresses and carbon enrichment associated with the bainite will reduce the rate of ferrite formation until the stresses are relaxed and the carbon diffused away at the higher temperature.

Partial bainite reaction at a higher temperature retards subsequent transformation at a lower temperature, and vice versa. The effect is more noticeable in higher-carbon steel. This effect is satisfactorily explained by the behaviour of the carbon. At higher temperatures the austenite adjacent to a bainite plate is enriched with carbon and so retards the bainite formation at a lower temperature, where such enrichment is not so great. Transformation at a lower temperature leaves less carbon nearby and so accelerates the transformation at a higher temperature. The differences in residual stresses in the temperature range for which data is available are of less importance than the carbon effect, as is evidenced by the larger variation with steel of higher carbon content.

Holding in the carbide range apparently retards slightly the subsequent formation of bainite. This has been explained as carbide nucleating at severe discontinuities and so rendering them unavailable for bainite nucleation. While this might be a contributing effect it must be noted also that the precipitation of carbides will harden the matrix, as in age hardening, and so make the shear reaction more difficult. A relationship has been suggested between the strength of the austenite and its stability in the lower transformation range.
Some data has been advanced on the effect of partial transformation on subsequent cementite precipitation. The data given indicate that holding in the bainite range for moderate fractions of the time necessary for 1% bainite to form retards the subsequent carbide precipitation, while holding for shorter times accelerates the precipitation. The latter effect appears more predominant with holding at a lower temperature in the bainite range. The retarding effect of moderate quantities of bainite has been explained by the utilization of nucleation sites by the bainite, reducing the number available for cementite nucleation. To explain why cementite was not nucleated on the cementite particles precipitated in conjunction with the bainite, the possibility of differing orientations of bainitic and proeutectoid cementite was advanced. Since there is no experimental evidence concerning the orientation of the cementite this must be considered as a possibility because of the different modes of formation. Accepting the depletion of nucleation sites by bainite, the effect of the carbides already present may be considered in the light of the mechanism of growth here advanced.

When the bainite is formed, the carbon content is increased in the adjacent region. Carbides are then precipitated at the interface, some of which at higher temperatures may redissolve. The remaining carbides will grow and cause a carbon depletion of the surrounding austenite, allowing the growth of the bainite near them. In this manner the cementite, originally on the austenite-ferrite interface, will become surrounded by ferrite. This process will occur more rapidly at higher temperatures.
The cementite particles surrounded by ferrite may be thought of as being made inactive as nucleation sites by the enveloping ferrite. This provides an explanation of the acceleration of subsequent cementite by short periods of holding in the bainite region, for, although the bainite will remove some sites of possible nucleation, it will provide many others if the time of reaction is not long enough to permit envelopment of the precipitated carbides. This effect is expected to be more noticeable at lower temperatures where the enveloping growth is much slower. In this regard it must be noted that the number of carbides precipitated in the initial stages of bainite formation is much greater than the number subsequently precipitated at the growing edges of the bainite. The accelerating effect of the quenching stresses will allow the effect of initial bainite formation by shear to predominate over the effect of the growing edges of bainite, since the amount of carbon entrapped (and hence the number of carbides precipitated at the interface) will be greater when the stresses promoting the shear are larger. As the internal stress becomes less controlled by the quench and more by the bainite formation the fluctuations in carbon may be expected to assist in the reaction, that is, the bainite will form in a region when the carbon concentration in that region fluctuates towards lower values. The formation of bainite under these conditions will tend less to cause adjacent regions of increased carbon concentration conducive to rapid carbide precipitation.
The initiation and course of the isothermal decomposition of austenite in the bainite region has been investigated, and a theory proposed to account for the observed phenomena associated with this transformation.

In the bainite region decomposition may take place by two mechanisms, (a) precipitation and growth by diffusion, and (b) phase change by martensitic shear. Since the shear reaction sets up residual stresses in the surrounding austenite and entraps carbon atoms, the free energy change of a region of austenite transforming to bainite by shear is of the form

\[ dG = dG_{Fe} + C dG_C - C T dS + dU \]

where
- \( dG_{Fe} \) is the free energy change of the iron in going from the f.c.c. structure to the b.c.c.
- \( dG_C \) is the difference in free energy between carbon in the f.c.c. lattice and carbon in the b.c.c. lattice.
- \( C \) is the carbon concentration
- \( T \) is the temperature
- \( dS \) is the change in entropy of the carbon
- \( dU \) is the strain energy associated with the transformation

The strain energy \( dU \) is such as to inhibit further transformation by shear along planes of similar orientation in the same austenite grain, and to assist transformation by shear along planes of certain complementary orientations. Since the activation energy of martensite-like reactions is negligible, the extension of a growing edge of a bainite plate by shear is assumed to occur
whenever the free energy of the adjacent austenite in the direction of growth may be reduced by the reaction. At any temperature, $dG_F$, $dG$, and $dS$ are independent of time, but $C$ and $dU$ are functions of the time and the progress of the transformation. $dU$ initially varies widely throughout the specimen because of quenching, is relaxed at a rate dependent upon the temperature, and is increased by the shear transformation. The progress of the shear reaction is thereby dependent upon the rate of stress relaxation. The carbon concentration will fluctuate with time by chance diffusion and by variations in internal stress conditions, will be increased by diffusion of carbon entrapped in bainite and decreased by precipitation of carbon as carbide.

Lattice coherency between bainite and the parent austenite is improbable except near the advancing edge of a bainite plate.

After the formation by shear of a region of bainite, carbon will diffuse out of the bainite into the surrounding austenite, locally enriching the austenite and precipitating highly-dispersed carbides at the disordered austenite-bainite interface. The carbon-enrichment will be greater at higher temperatures.

The decomposition of austenite in addition takes place through the growth of ferrite regions by diffusion of individual iron atoms from austenite to ferrite. Such a reaction has an associated activation energy, and its rate of reaction is restricted by the rate of diffusion of carbon away from the austenite-
ferrite interface. The rate of transformation of austenite by this means is proportional to the area of austenite-ferrite interface, and hence is highly dependent upon the amount of previously-formed sheared product.

Bainite is nucleated on the grain boundaries. The quenching stresses promote rapid initial nucleation. The shear reaction sets up inhibiting residual stress conditions which restrict the growth rate and number of operative nuclei.

The decomposition of austenite in the bainite region begins as a shear transformation. The lamellae formed by shear grow edgewise by continued shear until obstructed, as by grain boundaries, and sidewise by a diffusive process which causes them to agglomerate. The rate of the diffusive process decreases more rapidly with temperature than does the rate of the shear process. At higher temperatures the decomposition of austenite is initially by shear, but goes to completion by the diffusive reaction. At lower temperatures the decomposition progresses by the continued formation of new lamellae throughout the reaction period. The internal stresses set up by the shear transformation inhibit the growth of similarly oriented lamellae, which as the temperature is lowered and hence relaxation rate is decreased, reduces the tendency of parallel plates of bainite to occur in groups, as is to be expected from the effect of internal stress on nucleation.

A decrease in grain size accelerates the later stages of the decomposition of austenite in the upper bainite region, but has a negligible effect in the lower regions because the
rate of growth by shear is determined by the internal stress, not by the number of nuclei. The larger area of grain boundary provides a larger austenite-ferrite interface area, accelerating the decomposition by the diffusive process, which is predominant in the later stages of decomposition in the upper bainite range.

The proposed theory has been applied to account for the effects in the early stages of transformation observed with anisothermal transformation procedures.
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