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WATERTOWN ARSENAL LABORATORY

EXPERIMENTAL REPORT

NO. WAL. 310/37-2

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JUN 19 1981
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⑥ PRINCIPLES OF PHASE TRANSFORMATIONS
Third Partial Report, no. 3
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DISTRIBUTION STATEMENT A
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⑩ BY
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⑫ 84

⑭ WAL-310/37-2

⑪ DATE 25 January 1945

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1. Inclosed are sixteen copies of Report No. WAL 310/37-2, entitled "Principles of Phase Transformations, Third Partial Report". These reports are for distribution as follows:

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2. Copies of this report have also been sent to the Springfield Armory, Watervliet Arsenal, Rock Island Arsenal, Frankford Arsenal, Ordnance Research and Development Center and to certain other interested individuals.

3. In this report the principles are formulated which govern the decomposition of austenite. Many of the details of this decomposition are found to be deducible directly from theory, such as the interlamellar spacing of pearlite and the pearlite "C" curve.

For the Commanding Officer:N. A. MATTHEWS
Lt. Col., Ord. Dept.,
Assistant.2 Incls.
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25 January 1945

PRINCIPLES OF PHASE TRANSFORMATIONS

Third Partial Report

OBJECT

To formulate the general principles which govern the decomposition of austenite.

SUMMARY

An extended review of the results of this report is given as Part IV, where the results are applied to an interpretation of the time-temperature-transformation diagram. A brief review of the results is given below.

1. A review is given of the general principles which govern the phenomena accompanying the decomposition of austenite. These phenomena include nucleation, propagation of interfaces, grain growth and spheroidization.

2. The main features of pearlite formation are found to be derivable directly from fundamental principles. These features include: the variation of interlamellar spacing with temperature, the shape and the position of the pearlite "C" curve, the mechanism whereby strong carbide forming alloys retard the formation of pearlite.

3. The formation of bainite is interpreted as a transformation of the face-centered austenite lattice to the body-centered ferrite lattice without a change in carbon distribution.

4. Many of the characteristics of bainite and of bainitic formation are readily derivable from this interpretation. These characteristics include: the formation of only a limited amount of bainite at the highest transformation temperatures, the improvement in physical properties of low temperature bainite over high temperature bainite, the order of alloying elements arranged according to their effectiveness in retarding the formation of bainite.

5. Martensite is interpreted as having essentially the same structure as untempered bainite except that, due to

its mode of formation, residual stresses are present.

6. The manner in which alloying elements affect the formation of martensite is found to be such that, when arranged in the order in which they lower the A_r^h temperature, the order is the same as when arranged according to effectiveness in retarding the bainite transformation.

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H. 11.8.

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INTRODUCTION

The equilibrium relations in steels, the subject of the first and second partial reports of this series,¹ must form the basis for a scientific approach to the problem of the heat treatment of steel. From the equilibrium relations alone, however, practically nothing can be surmised regarding the mechanical properties of the steel. These properties depend primarily upon the mode of distribution of the two principal phases, ferrite and carbide. Even alloying elements affect the mechanical properties of steel largely through their influence upon the distribution of the ferrite and cementite.²

The initial stage in the heat treatment of steel is austenization. In this process the steel is heated to such a high temperature that (1) all the constituents become uniformly distributed, (2) the lattice structure is of the face-centered cubic type. The second stage is the cooling of the steel. The steel may then be used as is, or may be subjected to further heat treatment. In any case, the mechanical properties of the end product are largely conditioned by the mode of distribution of the cementite after the steel has been cooled from the austenitizing temperature. It is with the principles which determine this distribution in the as quenched steel before tempering that the present report, the third of this series, is concerned.

Although the reactions which occur on cooling are

essentially irreversible, none the less equilibrium relations play a fundamental role therein. The irreversibility resides primarily in the diffusion phenomena. The actual advance of a phase boundary is found to occur under essentially reversible conditions, the concentrations of the constituents being in equilibrium on the two sides of the boundary. Since diffusion obeys well known laws, the irreversible phenomena which accompany the cooling of steel from the austenitizing temperature are therefore susceptible to exact mathematical treatment.

I. GENERAL PRINCIPLES

A. Equilibrium Diagrams.

As is well known, many conventional equilibrium diagrams do not represent true equilibrium conditions. This is the case for the iron-carbon diagram as usually drawn, since cementite may decompose with the formation of graphite. Such a lack of true equilibrium in no way detracts from the usefulness of the conventional diagrams, since, when properly used, they do represent the actual equilibrium concentrations in the absence of nuclei of the more stable phase.

Caution must be used in the interpretation of equilibrium diagrams, even those representing true equilibrium. In such diagrams the implicit assumption is always made that the interface between two phases is a plane. In other words, surface tension is not taken explicitly into account.

When the interface is curved, as is always the case if one phase is dispersed and the other phase is continuous, the equilibrium concentrations are not those given by the equilibrium diagrams. The equilibrium relations must then be computed from first principles using the condition that any transfer of atoms must be accompanied by no change in free energy.

Equilibrium relations have physical significance even when the system as a whole is not in equilibrium, as when a new dispersed phase is growing in an undercooled continuous phase. As an example, the case of the growth of ferrite grains from a hypoeutectoid austenite will be considered. The advance of the phase boundary is accompanied by two distinct phenomena: (1) a shift in the position of each lattice atom so as to produce a body-centered structure from a face-centered structure; (2) a diffusion of carbon atoms away from the advancing interface. The shift of an iron atom on the austenite side of the phase boundary to the ferrite side of the phase boundary represents a movement which is relatively small compared to the movement of a carbon atom from one interstitial position to another. One therefore anticipates that the rate at which the ferrite grain grows will be determined solely by the diffusion of the carbon atoms and not by the transfer of the iron atoms from the austenite to the ferrite lattice positions, except of course in the case of very small carbon concentrations. According to this viewpoint, the position

of the phase boundary will be determined solely by the condition that the free energy be a minimum. The rate of advance is just such as to maintain the equilibrium concentration of carbon on the austenite side of the interface. How fast this rate of advance must be in order to maintain this equilibrium concentration depends in turn upon the rate at which the carbon diffuses away. According to the viewpoint herein adopted, the growth of one phase in another is therefore completely specified by the partial differential equations which govern diffusion, together with the condition that the phase boundaries move at such a rate as to maintain the equilibrium concentration just ahead of the advancing boundary,

The extensions of the phase boundaries into the so-called metastable regions have just as much physical meaning as do the phase boundaries themselves. Such extensions are illustrated in Figure 1 for the iron-carbon system. Thus suppose a hypoeutectoid steel of carbon concentration X_0 is quenched to the temperature T_1 . Free ferrite will then begin to grow. The composition of the austenite just ahead of an advancing ferrite grain with a plane boundary is then given by the value of the extension SG' at T_1 . Similarly if a hypereutectoid steel of composition X_0' is quenched to the temperature T_2 , free cementite will begin to grow. The carbon concentration in the austenite just ahead of an advancing cementite grain with a plane boundary

will be given by the value of the extension SE' at T_2 . Finally, if a nearly eutectoid steel is quenched to the temperature T_3 , both ferrite and cementite will begin to form. If the phase boundaries could be regarded as plane, the austenite just ahead of the advancing ferrite and of the advancing cementite grains would have the compositions given by the extensions SG' and SE' , respectively, at T_3 . The modification of the concentrations due to the finite curvature of the phase boundaries is of precisely the same nature as when the ferrite and cementite form above the eutectoid temperature where the conventional equilibrium diagrams are applicable.

B. Nucleation.

As has previously been mentioned, the condition for growth of a new phase is that such growth decrease the total free energy of the system, including the interface energy. This condition acts as a severe hindrance to the initiation of grains of the new phase. The mechanism of this restraint may best be illustrated for the case of a spherical grain. If the radius of a spherical grain increases from R to $R + \Delta R$, the ratio of the increase in volume to the increase in surface area is $(1/2)R$. Therefore the ratio of the free energy liberated by the volume transformation to the free energy needed to increase the interface varies as R . At any given temperature below the equilibrium temperature a critical radius will therefore

exist such that all the free energy liberated by the transformation is used up in increasing the area of the interface. If the radius is smaller than this critical value, the total free energy would be increased rather than decreased by growth. Grains having radii smaller than the critical value will therefore become smaller and finally completely disappear.

The above thermodynamical argument explains the difficulty of initiating the growth of a thermodynamically stable phase, a difficulty which is illustrated by the numerous well known examples of undercooling. A serious difficulty arises in understanding how a grain can ever attain its critical size, since, according to thermodynamics, smaller grains can only grow still smaller. The standard method of resolving this method is by means of the theory of nucleation.^{3,4}

According to the science of statistical mechanics, thermodynamics tells only what is most likely to happen, not what must happen. It is therefore possible, but perhaps very unlikely, that a grain may grow from atomic dimensions to the critical size in contradiction to the laws of thermodynamics. This probability may, in principle, be computed. It is proportional to $\exp \left\{ -G_c/kT \right\}$, where G_c is the free energy necessary to form the particle of critical size, and k is Boltzman's constant, 3.3×10^{-24} calories per $^{\circ}\text{C}$. Grains of the critical size are called

nuclei, and their formation is called nucleation.

Two properties of the nucleation factor $\exp \{-G_c/kT\}$ are of particular pertinence to the present discussion. The free energy G_c becomes infinite as the amount of undercooling becomes zero. The explicit expression for G_c may readily be shown ^(See Appendix B) to be

$$G_c = (16\pi/3) \cdot G_s^3 / (\Delta G_v)^2 \quad (1)$$

where G_s is the energy of the interface per unit area, and ΔG_v is the free energy liberated per unit volume by the transformation. The interface free energy is nearly independent of temperature, while the volume free energy is proportional to the amount of undercooling ΔT . Therefore

$$G_c \sim 1/\Delta T^2, \quad (2)$$

so the nucleation factor rapidly approaches zero as the amount of undercooling itself approaches zero. As a consequence, the rate of formation of a new phase is always zero just below the critical temperature, and increases to a maximum value at some finite amount of undercooling.

The second important property of the nucleation factor $\exp \{-G_c/kT\}$ is its extreme smallness. As a consequence of this smallness, nucleation will proceed in that manner in which the critical free energy is a minimum, however improbable such nucleation may seem. The condensation of water vapor may be cited as a familiar example of this deduction. The critical free energy of a water droplet is

much smaller when the droplet contains an electric charge than when it contains none. The path of a single high speed electron in a supersaturated vapor may therefore be detected by the droplets which condense about molecules ionized by the electron. Similarly the critical free energy of a precipitate from a solid solution is much smaller when the precipitate is adjacent to some imperfection than when it occurs in a perfect lattice. Grain boundaries constitute a common type of imperfection. As an example of the influence of grain boundaries in aiding nucleation, the case of cementite precipitating from eutectoid austenite will be considered. At 100° C below the eutectoid temperature, the critical free energy for a nucleus is 1.0×10^{-14} calories, provided the nucleus is completely surrounded by an austenite matrix (see Appendix B). For this case the nucleation factor is $10^{-1,300,000}$. If on the other hand, the nucleus is a hemisphere bounded on its plane side by a grain boundary, and if the interface energy is the same between the new and old phase as between two grains of the same phase, then the nucleation energy is only one half of its previous value. The grain boundary nucleation factor is therefore $10^{-650,000}$, which is $10^{650,000}$ times as large as for nucleation within the grain. The factor $10^{650,000}$ is so large as to ensure that nucleation will occur at the grain boundary rather than in the interior of a grain,

in spite of the fact that there are many more potential nucleation positions within the grain than on the grain boundaries.

C. Kinetics of Phase Boundary Propagation.

The advance of an interface boundary may involve only a change in lattice type, as in an allotropic transformation of a pure metal. The advance may also involve only a change in composition, as may occur when two elements of the same lattice types are completely soluble in one another at a high temperature but not at a lower temperature. Finally, the advance of an interface boundary may involve both a change in lattice type and also a change in composition. This last case is the most common of the three, and is the only case which will be discussed here. In this discussion only a single solute will be assumed to be present.

If the phase boundary remained stationary, the ratio of the concentration of solute atoms on the two sides of the interface would rapidly approach the equilibrium ratio, i.e.,¹

$$C_2/C_1 = (\beta_2/\beta_1)e^{-(G_2-G_1)/kT} \quad (3)$$

In this equation the subscript refers to the phase, β is unity in the case of substitutional solutes, is equal to the ratio of interstitial positions to lattice atoms in the case of interstitial solutions, and G refers to the

atomic free energy¹ of the solute per atom. If the phase boundary advances sufficiently rapidly, there is not time for an appreciable change in concentration on the two sides of the interface, and the concentration of the solute remains unchanged.

The equilibrium ratio is essentially maintained whenever the rate at which the phase boundary advances is limited primarily by the rate of diffusion of the solute atoms away from or towards the advancing phase boundary. This situation appears to arise in the high temperature decomposition of austenite into free ferrite, free cementite, or into pearlite. The phase boundary can advance without any change in composition only when the temperature is sufficiently low so that the free energy of the system is decreased by such advance. As is discussed later, this situation arises in the formation of low temperature bainite. It is also possible that the phase boundary advances at such a rate that the equilibrium ratio of solute concentration on its two sides is partially but incompletely attained. It will later be shown that this is the situation in the formation of high temperature bainite. In such an intermediate case the kinetics of the phase boundary advance is especially complex. The simpler case of complete equilibrium on the two sides of the phase boundary is discussed in detail below.

The variation of the solute concentration on the two sides of an advancing phase boundary is shown schematically

in Figure 2. In computing the velocity of the phase boundary, V_B , the simplifying assumption will be made that the density of the solvent atoms is essentially the same in the two phases. We shall let the concentrations C_1 and C_2 refer to the number of solute atoms per unit volume of the two phases. The current density of atoms in the old phase away from the phase boundary is then given by

$$\text{current density} = (C_2 - C_1)_B V_B ,$$

where current density refers to the net number of solute atoms which cross a unit area in unit time. The current density may also be expressed in terms of the atomic diffusion coefficient D by the following equation

$$\text{current density} = -D(\delta C_2 / \delta X)_B$$

where X refers to the coordinate normal to the phase boundary, and whose positive axis extends into the old phase. Upon combining the above two equations for the current density, one obtains

$$V_B = \frac{-D}{(C_2 - C_1)_B} \cdot (\delta C_2 / \delta X)_B . \quad (4)$$

In certain cases, such as in the growth of cementite, the concentration C_1 is fixed. In other cases, such as in the growth of ferrite, this concentration is to some extent indeterminate. The only unavoidable restriction upon C_1 is that it be such that in no element of volume can the free

energy be increasing. Upon applying this restriction to an element containing the interface, it is found in Appendix A that

$$(C_2 - C_1)_B = \Delta G/kT, \quad (5)$$

where k is Boltzmann's constant, and ΔG is the free energy liberated by the transfer of a unit volume of solvent from phase #2 to phase #1. When the equality sign is valid in Equation (5), no free energy is dissipated at the interface boundary itself as the boundary advances, all the free energy is dissipated by the diffusion of the solute atoms ahead of the advancing boundary. Reference to Equation (4) and to Figure 2 shows that the gradient of C_2 at the boundary increases in magnitude with $(C_2 - C_1)_B$ faster than $(C_2 - C_1)_B$ itself. The velocity of the phase boundary may hence be seen from Equation (4) to have a maximum value when the equality sign in Equation (5) is valid. This equality sign in Equation (5) will therefore be assumed to be valid unless special consideration demands otherwise, i.e.,

$$(C_2 - C_1)_B = \Delta G/kT, \quad (6)$$

It is to be noted that Equations (3) and (6) are just the equations which determine the concentration of the solute in two phases when they are in absolute equilibrium.

D. Kinetics of Growth of New Phase.

The general principles which govern the growth of a

new phase into an old phase have been discussed by Carpenter and Robertson.⁵ In the present section the principles which they clearly enunciated are presented in a more quantitative form than heretofore.

The velocity with which every part of the phase boundary propagates is given by Equation (4). In this equation the concentration gradient $(\delta C_2 / \delta X)_B$ may be represented as the ratio

$$-(\delta C_2 / \delta X)_B = \Delta C / L . \quad (7)$$

Here ΔC is the difference in carbon concentration in the parent phase just at the advancing boundary and far away from the boundary. It is this concentration difference which gives rise to diffusion. The quantity L has dimensions of length, and will in every case be related to some linear dimension of the advancing phase.

Upon combining Equations (4) and (7), one obtains

$$V_B = \frac{\Delta C}{(C_2 - C_1)_B} (D/L) . \quad (8)$$

Since in this equation the concentrations occur only as a ratio, they may be expressed in any desired units.

From Equation (8) one may reach certain conclusions regarding the shape of a growing grain, conclusions which may also be reached from general considerations upon diffusion.⁶ If the phase boundary were a plane of such large extent that diffusion was everywhere normal to the

plane, the effective diffusion distance L would gradually increase, thereby lowering the velocity of growth. On the other hand, if the phase boundary is convex towards the parent phase, as is usually the case, the effective diffusion distance L will be comparable to the radius of curvature of the surface. From this fact one therefore deduces that the smaller the radius of curvature the more rapid the rate of growth. If a grain grew as a spheroid, its linear rate of growth would gradually decrease as its size, and hence the radius of curvature of its surface, increased. On the other hand, a plate may grow edgewise and maintain a constant radius of curvature at the growing surface, and therefore also a constant rate of growth. The rate at which the thickness of such a plate increases will gradually decrease with time, as previously explained. An initially platelike grain will therefore remain platelike. On the other hand, a growing spheroidal grain will not remain spheroidal, for the slightest fluctuation from a spherical form will grow, resulting finally in a plate. This facility with which plates grow edgewise compared with the radial growth of spheroids explains the nearly universal occurrence⁷ of platelike structures in the initial stage of precipitation in solid solutions.

One might surmise from the preceding discussion that the radius of curvature of the edge of a plate would continually decrease as it advanced. A lower limit to this

radius of curvature is imposed however by the change in equilibrium relation with change in curvature of the interface. The example of a free cementite plate growing in austenite is shown in Figure 3. It is supposed that when the steel is at a high temperature T_0 it has a homogeneous austenite structure of carbon concentration X . When the temperature is now lowered to T_1 , the concentration of carbon in the austenite which is in equilibrium with the cementite is $X - \Delta C_0$, provided the interface is plane. The maximum concentration difference in the austenite just at the interface and further away is therefore ΔC_0 . On the other hand, if the interface is convex towards the austenite, as it must be if the cementite is growing, the boundary of the gamma phase is lower than for a plane interface, and therefore the concentration difference is less than ΔC_0 . Since for small curvatures of interface the shift in boundary is proportional to the curvature, the concentration difference is given by

$$\Delta C = (1 - r_0/r) \Delta C_0, \quad (9)$$

where r_0 is the critical radius of curvature at which the concentration difference is zero. Upon combining Equations (8) and (9), one may now determine what curvature the edge of an advancing plate approaches. This limiting curvature will be such as to make the velocity of advance V_B a maximum. Since the effective diffusion distance L is proportional to the radius of curvature r , the radius of

curvature will approach that value which maximizes the ratio $(1 - r_0/r)/r$. This value is $2r_0$.

Reference to Figure 3 shows that when the radius of curvature of the interface is $2r_0$, the amount of undercooling is exactly half its value for a plane interface. Since the change in free energy is proportional to the amount of undercooling, we conclude that as the plate advances, only one half the available free energy is irreversibly dissipated in diffusion, the other half remaining as interface energy.

We are now in a position to determine how the velocity varies with temperature. The concentration difference ΔC that causes diffusion in the parent phase is proportional to the amount of undercooling ΔT . The effective diffusion distance L is proportional to r_0 , which in turn is inversely proportional to ΔT . Finally, the diffusion coefficient varies with temperature as

$$D \sim e^{-Q/RT} \quad (10)$$

Upon combining these three factors, we obtain from Equation (8)

$$v_B \sim (\Delta T)^2 e^{-Q/RT} \quad (11)$$

This velocity is very small at small amounts of undercooling, due to the small concentration difference ΔC which drives the diffusion, and to the large distances over which diffusion must occur. It is also very small for larger amounts

of undercooling due to the slow rate of diffusion at low temperatures. An intermediate amount of undercooling exists at which V_B is a maximum.

E. Spheroidization.

If only a single grain were growing in a matrix, it would continue to extend indefinitely. That portion which was extending the most rapidly would maintain a constant radius of curvature, namely twice the critical radius r_c . The growing grain would therefore maintain a platelike shape. In all actual cases neighboring growing grains will eventually impede growth. Such an impediment may be taken account of phenomenologically by considering the concentration of the parent matrix to be gradually changing. If the growing phase can be regarded as a precipitate, such as cementite, the concentration of the parent phase may be regarded as gradually decreasing. Such a decrease in concentration will eventually lead to the spheroidization of the original plates, even though the temperature be maintained constant. The mechanism of such spheroidization is discussed below.

The process of spheroidization may best be described by reference to Figure 4. In this figure are drawn the boundaries of the parent phase for a series of values of the radius of curvature of the interface, the curvature being taken as convex towards the parent phase. The uppermost boundary corresponds to a plane interface, the

lowermost boundary to an interface with the critical radius of curvature for the concentration X_0 and temperature T^1 . If now the temperature of the parent phase with concentration X_0 is suddenly lowered to, and maintained at T^1 , the radius of curvature of the advancing phase will be $r_0 = 2r_c$, as previously explained. This radius of curvature is that for which the rate of growth is a maximum. As growth proceeds, the concentration of the surrounding parent phase is gradually reduced by the growth of neighboring grains. The critical radius of curvature, as well as the actual radius of curvature, will therefore increase. Thus when the concentration has been reduced to X_1 , the actual radius of curvature is increased to r_1 , etc.. As growth proceeds, and the concentration of the parent phase becomes reduced, the critical radius of curvature will increase so fast that the actual radius of curvature will begin to lag behind the radius for maximum rate of growth, namely twice the critical value. Finally the critical radius of curvature will become equal to the actual radius. At this time growth ceases at the edges. Further growth can then proceed only upon the faces. As the critical radius of curvature further increases, the edges begin to dissolve. Spheroidization has then commenced.

II. PURE IRON-CARBON SYSTEM

A. Formation of Pearlite.

The manner in which a single ferrite or a single cemen-

tite grain grows isothermally depends markedly upon whether the temperature of growth is above or below the eutectoid temperature. If a ferrite grain grows above the eutectoid temperature, the carbon concentration of the austenite immediately surrounding the growing grain is along the boundary GS in Figure 1, and is therefore not sufficiently high for cementite nuclei to form and grow. The grains will therefore grow indefinitely, ^{until impeded by neighboring grains.} On the other hand, if the temperature is below the eutectoid, the carbon concentration in the austenite immediately surrounding the grain lies upon SG', and is therefore sufficiently high for the formation of stable cementite nuclei. Similarly, a cementite grain growing above the eutectoid temperature ^{until impeded by neighboring grains,} can continue to extend indefinitely, while below the eutectoid temperature it will eventually become surrounded by ferrite. The growth of either a ferrite or of a cementite grain below the eutectoid temperature cannot at present be adequately described, since the theory for nucleation in the surrounding austenite has not been developed.

If the temperature is below the eutectoid, and the carbon concentration lies between SE' and SG', ferrite and cementite nuclei may form and grow simultaneously. In such cases the cementite and ferrite grow as parallel plates, and form what is known as pearlite. The laws of formation of pearlite are described in the following sections.

1. Interlamellar Spacing.

The temperature variation of interlamellar spacing in pearlite of eutectoid composition has been the subject of careful experimental study by Mehl and his collaborators.⁸⁻¹² The pearlite which forms just below the eutectoid temperature has comparatively large spacing. This spacing decreases continuously as the temperature of formation is lowered. The pearlite finally becomes so fine as to be unresolvable by the microscope,

The minimum possible interlamellar spacing S_0 in pearlite formed isothermally may be computed by pure thermodynamic methods. From the arguments presented in a previous section, it may be deduced that that pearlite grows most rapidly in which the spacing is twice this minimum spacing.

In the computation of S_0 one inquires as to what is the condition that the free energy of the complete system be lowered by the growth of a pearlite nodule. This condition is that the free energy released by the transformation be more than sufficient to supply the energy associated with the interface between the cementite and the ferrite plates. In order that this condition may be expressed in a precise mathematical form, a pearlite nodule of interlamellar spacing S_0 is considered to be advancing into the parent austenite, as illustrated in Figure 5. An equation will be set up which says that as the nodule

grows the free energy remains unchanged in a region which includes one cementite and one ferrite plate. This volume is indicated by dotted lines in Figure 5, and will be considered to have the depth \underline{W} . When the nodule advances a distance dX , the volume of austenite transformed in the region under consideration is $S_0 \cdot W \cdot dX$, and therefore the mass of the austenite transformed is $\rho S_0 \cdot W \cdot dX$, where ρ is the density. The free energy which is available for the formation of new interfaces is therefore

$$\text{available free energy} = L_{\text{mass}} \cdot \frac{T_e - T}{T_e} \cdot \rho S_0 \cdot W \cdot dX, \quad (11a)$$

where L_{mass} is the heat of transformation per unit mass. The increase in the total interface area is $W \cdot 2dX$. Upon taking S as the surface energy per unit area, the increase in interface energy is given by

$$\text{increase in interface energy} = 2S \cdot W \cdot dX. \quad (11b)$$

Upon equating the available free energy to the increase in interface energy, one therefore obtains

$$L_{\text{mass}} \cdot \frac{T_e - T}{T_e} \cdot \rho S_0 = 2S. \quad (12)$$

The solution of this equation for the interlamellar spacing gives

$$S_0 = \frac{2T_e S}{\rho L(T_e - T)}. \quad (13)$$

According to Equation (13), the interlamellar spacing is inversely proportional to the amount of undercooling. Therefore a plot on log paper of the interlamellar spacing vs. the amount of undercooling should give a straight line with a slope of -1. Such a plot is given as Figure 6 of the data from reference 11 for a eutectoid steel. The data are seen to be consistent with equation (13).

By extrapolation one surmises from Figure 6 that if pearlite could form at the absolute zero, its interlamellar spacing would be of the order of magnitude of 200 Angstroms. This conclusion is in violent contradiction to the view of Mehl⁸ that the interlamellar spacing has a heat of activation, and approaches atomic dimensions at temperatures not far below the nose of the S curve. The same data which were plotted in Figure 6 have also been plotted in Figure 7 according to Mehl's viewpoint, i.e., the log of S_0 vs. $1/T$. The experimental points fall upon a straight line in this graph just as well as in Figure 6. The extrapolation of this plot to lower temperatures gives however radically different results than the extrapolation in Figure 6. Thus at 400° C the interlamellar spacing is given as one Angstrom. A comparison of Figures 6 and 7 illustrates the danger of extrapolating a formula which fits experimental data over a limited range, but which has no sound theoretical basis.

One may now use Equation (13) to compute the interface energy density S . In this equation S_0 refers to the

minimum interlamellar spacing which allows growth. As has previously been mentioned, those nodules grow most rapidly whose interlamellar spacings are twice the minimum. Therefore the spacings given in Figure 5 may be considered as twice the minimum spacing. The equation of the straight line in this figure is then

$$2S_0 \cdot (T_e - T) = 0.0017 \text{ cm } ^\circ\text{C} \quad (14)$$

The experimental value for the heat of decomposition of a eutectoid austenite is¹³

$$L_{\text{mass}} = 20.5 \text{ cal./gram} \quad (15)$$

Substitution of Equations (14) and (15) into Equation (13) leads to

$$S = 6.8 \times 10^{-5} \text{ cal/cm}^2 = 2,800 \text{ dynes/cm} \quad (16)$$

This surface tension of cementite in alpha iron is nearly twice the reported¹⁴ macroscopic surface tension of steel in air, namely 1500 dynes/cm.

2. Pearlite "C" Curve.

A clear picture of the kinetics of the edgewise growth of a pearlite nodule was first presented by Hultgren,¹⁵ and is shown in Figure 8. The concentration of carbon in the austenite is greater just ahead of the ferrite than just ahead of the cementite. This difference in concentration results in a diffusion current of carbon in the austenite

from the ferrite interface to the cementite interface, as indicated in this figure.

Since a growing pearlite nodule does not appreciably change the carbon concentration of the surrounding austenite at distances greater than one interlamellar spacing, neighboring pearlite nodules do not influence each other's growth until they impinge upon one another. Their rate of growth is therefore constant. In the particular case where nucleation at the grain boundary is infinite, i.e. when the boundary upon undercooling instantly becomes covered with pearlite growing inwards, the time for completion of the reaction in an austenite grain is given by

$$\tau = \frac{\text{Radius of Grain}}{\text{Velocity of Growth}} \quad (17)$$

Upon observing that the heat of activation for diffusion of carbon in austenite^s is 36,000 cal./mole, one therefore obtains from Equation (10) for a eutectoid steel,

$$v \sim e^{-18,000/T} (T_e - T)^2 \quad (18)$$

where T_e is the eutectoid temperature. A plot of this equation is presented as Figure 9. This theoretical "C" curve for infinite nucleation rate is precisely of the same shape as observed. The nose of this theoretical curve occurs slightly above the temperature of the nose of the observed "C" curve for eutectoid plain carbon steels. If due account were taken of the fact that the rate of

nucleation is not infinite, the upper portion of the pearlite "C" curve would be displaced to the right relative to the lower portion. This relative shift would lower somewhat the temperature of the nose, thereby bringing the theoretical "C" curve into better agreement with the experimental "C" curve.

The horizontal position of the nose of the "C" curve may be computed from Equation (8). The numerator of the first factor refers to the excess in concentration of carbon in the austenite just ahead of the ferrite over that just ahead of the cementite plates. At the temperature where the theoretical "C" curve is at a minimum, namely 630° C, this concentration difference is 1.4%. At this temperature the denominator of the first factor, namely the excess of carbon concentration in the cementite over that in the austenite just ahead of cementite, is 6%. The first factor is therefore 0.23. The thermal diffusion coefficient of carbon in austenite at 630° C may be estimated by an extrapolation of the data of Wells and Mehl.¹⁶ From Figure 10 this extrapolation is seen to give the value 2.5×10^{-9} cm²/sec. The effective diffusion distance L will be related to the interlamellar spacing S_0 . We shall set

$$L = \alpha S_0 \quad , \quad (19)$$

where α is a numerical coefficient. Although the velocities

of the ferrite and of the cementite plates must be equal, the individual factors in Equation (8) depend upon which type of plate is under consideration. When, as in the present case, the cementite plate is considered, the effective diffusion length L will be comparable to the thickness of a cementite plate, so that the coefficient α will be comparable to 0.12. Finally, upon taking from Figure 6 the interlamellar spacing at 630° C as 1.8×10^{-5} cm, we obtain

$$V_B = (3.2 \times 10^{-5}/\alpha) \text{ cm/sec} \quad (20)$$

as the velocity at which a pearlite nodule advances at 630° C.

The time for the completion of the reaction may now be obtained by substituting Equation (20) into Equation (17). For an A.S.T.M. grain size of 4-5, the radius of the average grain¹⁷ may be taken as 0.004 cm. For such a grain size the time for completion of the pearlite reaction is, according to Equations (17) and (20),

$$\tau = 120 \alpha \text{ secs.}$$

The experimental value¹⁸ for the completion time at the nose of the "C" curve for a plain carbon steel (0.3% Mn) of this grain size is 5 secs. In order to bring the theoretical and experimental times for completion into agreement, it is necessary that the numerical constant α be 0.04, one

third the value obtained by identifying the effective diffusion distance with the cementite plate thickness. This value of α is sufficiently close to that predicted from general considerations so that one can be confident that the picture of growth herewith presented is essentially correct. A precise computation of the time of completion would involve a precise computation of the velocity of growth V_B , which in turn would require the precise determination of the shape of the cementite-austenite and of the ferrite-austenite interfaces, and the solution of the differential equations for carbon diffusion from the advancing ferrite plates to the advancing cementite plates.*

B. Bainite Formation.

As previously mentioned, the only condition that must be satisfied for the growth of a new phase is that such growth be attended by a decrease in the total free energy of the system. It is not at all necessary that the old or new phases be in equilibrium with one another, or that the end product be in a condition of stable equilibrium. Any type of phase change whatsoever may occur provided such a change be accompanied by a decrease of free energy. In other words, that phase change which does occur is not

*Such a computation has been carried out by W. H. Brandt, and is to be published in the Journal of Applied Physics.

necessarily that phase change which decreases the free energy the most, but rather that which proceeds at the greatest rate. As one example of the above statement the formation of pearlite may be cited. Here the end product has a much higher free energy in the form of interface energy than it need have. However, the end product which forms is that product which forms the most rapidly. Another example occurs when a solid solution suffers a change in phase without a change in composition. The transformation of austenite without a change in composition is discussed in detail below.

As mentioned above, the only condition necessary that a transformation proceed is that the free energy be decreased thereby. If one mole of iron, in which is dissolved C moles of carbon, transform from austenite to ferrite of the same composition, the change in free energy of the system is

$$\Delta G = -\Delta G_{Fe}^{\alpha \rightarrow \gamma} + C \Delta G_C^{\delta \rightarrow \alpha} - C T \Delta S_C^{\delta \rightarrow \alpha} . \quad (21)$$

In this equation $\Delta G_{Fe}^{\alpha \rightarrow \gamma}$ is the excess of free energy of one mole of pure iron in the austenite phase over that in the ferrite phase, and is given in table A-1 of reference 1; $\Delta G_C^{\delta \rightarrow \alpha}$ is the excess of atomic free energy of one mole of carbon when dissolved in alpha iron over that when dissolved in gamma iron, and is approximately 9,600 cal./mole; and $\Delta S_C^{\delta \rightarrow \alpha}$ is the excess of entropy of one mole of

carbon when dissolved in austenite, which, from considerations given in Reference 1, may be seen to be $R \ln 3$. Upon setting $\Delta G = 0$, one obtains an equation for the critical temperature below which the austenite may transform into ferrite of the same carbon concentration. This equation may be most conveniently solved for the atomic carbon concentration C in terms of the critical temperature. This equation is

$$C = \frac{\Delta G_{Fe}^{\alpha}}{\Delta G_c^{\gamma \rightarrow \alpha} - T \Delta S_c^{\gamma \rightarrow \alpha}} \quad (22)$$

A plot of Equation (22) is given in Figure 11 as the upper boundary of the shaded band. The lower boundary of the shaded region represents the same equation in which $\Delta S_c^{\delta \rightarrow \alpha}$ has been set equal to zero. The shaded region itself represents the uncertainty which exists as to whether the change in entropy of the carbon atoms should or should not be considered. There can be no doubt but that this entropy change should be considered if the transformation proceeds sufficiently slowly, as is certainly the case when the new phase arises through grain growth. When, however, comparatively large regions transform, by some sort of lattice distortion, in a time short compared to the time required for the carbon atoms to jump from one interstitial position to another, then the entropy term should not be considered.

The ferrite which forms from austenite without a change in carbon concentration is to be identified as bainite, or perhaps more properly as bainite before any carbon diffusion has occurred. The diffusion of carbon within bainite during its formation leads to a diversity of structures. These are described below.

At the highest temperature at which the bainite reaction can proceed, the diffusion rate of carbon is still fairly high in the austenite. It is expected to be much higher in the ferrite because in the body-centered lattice the interstitial positions are fairly close to one another, and therefore the potential energy hill separating adjacent positions should be comparatively low. This diffusibility of the carbon will result in the carbon diffusing out of a growing ferrite grain into the surrounding austenite matrix where the free energy for carbon is lower. This increase of carbon concentration in the surrounding austenite will however result in a lowering of the critical temperature for the formation of bainite. As this critical temperature is lowered to the temperature at which the steel is being held, the transformation stops, as is indeed the case under isothermal conditions at the highest temperatures of bainite formation.¹⁹ Further transformation may then be obtained only by a lowering of the temperature. Such increase in amount of transformation with a lowering of the temperature has been frequently reported in the literature.²⁰ ~~Such precipitation of a~~

~~cementite film surrounding a ferrite plate is commonly observed in bainite formed in the high temperature range.~~²¹

The enhancement of carbon concentration in the austenite immediately surrounding the bainite grain may likewise lead to the precipitation of a cementite film surrounding the bainite, thereby preventing further growth even at lower temperatures.²¹ An example of a bainite grain whose growth was so impeded is shown in illustration a of Figure 14.

Suppose, on the other hand, that the bainite is formed at such a low temperature that the carbon cannot diffuse out of a growing bainite grain. If the steel is then maintained at the transformation temperature for a sufficiently long time, or if it is elevated for a shorter time, the carbon will precipitate as cementite. The initial distribution of the cementite will, as discussed in the section on Growth, be in the form of plates. An example of such a platelike distribution is shown in illustration b of Figure 14. If the steel is held at the transformation or at a higher temperature for a sufficiently long time, the individual plates will spheroidize, as explained in the section on spheroidization. These spheroids will be grouped on planes corresponding to the original plates. Such a grouping of cementite spheroids may be seen in the illustrations of Davenport.²²

In the previous section upon rate of pearlite formation, the difficulties inherent to the computation of nucleation rates were circumvented by the assumption of infinite nucleation rate at the boundaries. In the case of bainite,

where to a large extent the nucleation takes place in the interior of the grains, no such simplifying assumption can be made. In order to obtain even a rough estimate of the rate of bainite formation, some estimate would have to be made of the rate of nucleation. The theory has not yet been developed from which such an estimate could be made. The extensive experimental work of Wever and his school (Kaiser-Wilhelm-Institut für Eisenforschung) upon the rate of formation of bainite cannot therefore at present be compared with theory.

C. Formation of Martensite.

It is well recognized that martensite forms from austenite by some sort of shear mechanism. Whatever the mechanism, the free energy of the end product must certainly be smaller than the free energy of the initial austenite. In computing this change in free energy, the slight distortion of the martensite from the cubic lattice will be neglected, aside from possible elastic strains. Since the individual martensite needles form so very rapidly, the carbon atoms cannot be considered as undergoing a change in entropy during the transformation. The last term in Equation (21) must therefore be omitted. However, by the very mechanism by which the martensite forms, the lattice must be left in a stressed condition. An additional term must therefore be added to Equation (21) to take account of this strain energy. If ΔU denotes this strain energy per mole of transformed iron,

Equation (21) becomes

$$\Delta G = -\Delta G_{Fe}^{\alpha \rightarrow \delta} + C \Delta G_C^{\gamma \rightarrow \alpha} + \Delta U . \quad (23)$$

As for bainite, the critical temperature for the formation of martensite is obtained by equating ΔG to zero. The resulting equation may be most readily solved for the atomic carbon concentration C . This equation is

$$C = (\Delta G_{Fe}^{\alpha \rightarrow \delta} - \Delta U) / \Delta G_C^{\gamma \rightarrow \alpha} . \quad (24)$$

Complete agreement with experiment is obtained¹ for the critical temperature for martensite formation, the A_r'' temperature, by taking the strain energy as a constant independent of carbon concentration. The energy is found to be

$$\Delta U = 357 \text{ cal./mole} . \quad (25)$$

If the strain energy were to be concentrated in the martensite itself, and if no plastic deformation relieved the stress, the stress corresponding to this value of ΔU would be 1,500,000 psi. The assumption of constant strain energy may seem contradictory to experience, since it is known that the higher the carbon content the higher are the residual stresses. This observation is not, however, contradictory to the assumption of constant strain energy, for the martensite of low carbon concentrations forms at a comparatively high temperature where high stresses are quickly relieved through plastic deformation.

The continual lowering of the martensite transformation temperature by the transformation itself finds a ready interpretation in the hypothesis that the interference of martensite needles already formed with the needles being formed raises the strain energy ΔU needed for further transformation.^{1,5}

D. Transition of Tetragonal to Cubic Martensite.

In the previous section martensite was considered simply as supersaturated ferrite. As was first recognized by Fink and Campbell,²³ the lattice of freshly formed martensite differs from the body centered cubic structure of ferrite in that one principal axis is elongated slightly with respect to the other two principal axes. Fink and Campbell likewise found that the slight tetragonality is removed by tempering at temperatures as low as 100° C. Bain²⁴ has pointed out that the tetragonality of freshly formed martensite is due to the restraints imposed by the carbon atoms upon the transformation of a face centered to a body centered cubic lattice. Honda and Nishiyama²⁵ have shown how the loss of tetragonality of freshly formed martensite results from the transition of the carbon atoms from their original positions to neighboring equilibrium positions. One of the foremost authorities²⁶ upon tempering in this country does not accept the conclusions of Honda and Nishiyama, no doubt because of their rather unconvincing arguments. Even the existence of the change of tetragonal into cubic martensite has

been thrown into disrepute. It is therefore believed profitable to re-examine the phenomenon of loss of tetragonality from a fresh viewpoint.

In order to prepare a background for the study of the mechanism of loss of tetragonality, it is necessary first to discuss in detail the reasons why freshly formed martensite is tetragonal. It is generally recognized that martensite forms from austenite by some sort of lattice shear strain which is homogeneous over macroscopic regions of the lattice. The precise nature of the shear strains, which has been a matter of dispute,²⁷ is immaterial to the present discussion, since any homogeneous shear strain may be represented as the superposition of three tensile strains along three orthogonal axes, and of a rotation of axes.²⁸ Therefore, irrespective as to the precise nature of the shearing strains, the distortion of the lattice, as distinct from its reorientation, may be represented by simple tensile strains along the principal axes. As Bain²⁴ has pointed out, this distortion is a contraction along one principal axis and extensions along the other two.

In the face centered austenite lattice each interstitial position has six iron atoms as closest neighbors. These six iron atoms are situated at equal distances along the three principal axes passing through the interstitial positions. As the lattice is now distorted from the face centered cubic to the body centered cubic type, the iron atoms surrounding

each interstitial position no longer remain at equal distances. The two neighboring iron atoms on the axis of compression, the tetragonal axis, come closer to the interstitial position than the other four neighboring iron atoms. A carbon atom in an interstitial position will therefore exert a greater pressure along the tetragonal axis than along the transverse axes. The cubic structure is therefore destroyed by distortions caused by the dissolved carbon atoms.

Some uncertainty exists as to whether the interstitial positions of the face centered lattice transform into stable or into unstable interstitial positions of the body centered lattice. This uncertainty is a reflection of the uncertainty as to which are the stable interstitial positions of the body centered lattice. In the present discussion they will be assumed to be at the center of the faces and edges of the unit cube. According to this viewpoint, when a face centered cubic lattice is transformed into a body centered cubic lattice, the interstitial positions remain as interstitial positions, but lose their cubic symmetry, having a smaller dimension along the tetragonal transformation axis than along the transverse directions. The interstitial lattice as a whole must however have cubic symmetry. This comes about from the opening up of new interstitial positions during the transformation from the face centered to the body centered cubic lattice. Analysis shows that for every initial

interstitial position two new interstitial positions appear, one with its tetragonal axis along a principal axis of the body centered lattice which is normal to the tetragonal transformation axis, the other interstitial position with its tetragonal axis along the other axis normal to the tetragonal transformation axis. However randomly distributed the carbon atoms may have been in the original austenite matrix, in the freshly formed martensite they are no longer randomly distributed in the interstitial positions. They only occupy those positions whose tetragonal axes are parallel to the tetragonal transformation axis.

The interstitial positions of a body centered cubic lattice are here considered to be at the centers of the faces and of the edges of the unit cells. Each interstitial position therefore has four nearest interstitial positions as neighbors. Inspection shows that the tetragonal axes of their nearest neighbors are normal to that of the interstitial position under consideration. Therefore as soon as two thirds of the carbon atoms migrate to the neighboring interstitial positions, the carbon atoms will acquire complete randomness in their distribution, and the lattice will then have lost all traces of tetragonality. Since the first stage of tempering must consist of the migration of carbon atoms to the neighboring interstitial positions, the conclusion is unavoidable that tetragonal martensite must change to a body centered ferrite with all the originally dissolved carbon still

in solution, before any precipitation or intermediate phase can form.

The above interpretation of the mechanism of loss of tetragonality differs slightly from that given by Honda and Nishiyama in that they assumed the interstitial positions of the face centered lattice transform to positions of unstable equilibrium. The transition from such unstable to stable equilibrium positions would, they show, be accompanied by a loss of tetragonality. A decision as to which viewpoint is correct can be made experimentally. If the viewpoint adopted in this paper is correct, then the time-temperature relation for the disappearance of tetragonality will be given by a heat of activation identical to the heat of activation for the diffusion of carbon in ferrite. If the viewpoint of Honda and Nishiyama is correct, the tetragonality will disappear much faster than would be expected from the rate of diffusion of carbon.

As was pointed out by Bain, the tetragonal lattice may be regarded as an intermediate stage in the transition from the austenite to the ferrite lattice. It is therefore also to be expected that the residual shear strains in freshly formed tetragonal martensite are less than those in the cubic martensite which results from low temperature tempering. The consequent increase in residual shear strains which accompanies tempering at low temperature explain several apparently unrelated phenomena. These phenomena are dis-

ussed below.

i. Freshly formed martensite is made more reactive to etching reagents by tempering at 100° C. This change in etching character is what would be expected by an increase in the residual shear stresses.

ii. More austenite remains untransformed when the steel is quenched slowly than when quenched rapidly. Unless the steel is quenched extremely rapidly, much of the martensite which is initially formed transforms into the cubic structure. The resulting increase in residual shear stresses will tend to hinder the formation of further martensite just as the formation of tetragonal martensite tends to hinder the formation of further martensite.

iii. Holding martensite at room temperature for a long time renders it more difficult to transform the remaining austenite by sub-atmospheric treatment. Here as in the previous case, the explanation is to be found in the increase in residual shear stresses accompanying the transition from tetragonal to cubic martensite.

If martensite is given too high a temper, all residual stresses will be relieved. This relief of stresses may be the explanation as to why some of the austenite retained on the original quench will transform if heated to moderate temperatures and is then requenched.

III, EFFECT OF ALLOYS UPON DECOMPOSITION OF AUSTENITE

According to the way in which alloying elements affect

austenite decomposition, they may be divided into two classes. The elements of one class have qualitatively the same effect upon the S curve as has carbon itself. These elements retard the formation of both pearlite and bainite by about the same amount, and also lower the temperature for the initiation of martensite. Mn and Ni are the most common elements of this class. The elements of a second class retard the formation of pearlite much more than the formation of bainite. Molybdenum is the most outstanding example of this class. It thus appears that each alloying element has two characteristic properties, one of which has a moderate effect upon retarding all types of austenite decomposition, the other of which has a specific influence upon pearlite formation.

A. Pearlite.

The specific effect of alloying elements of the second class in retarding pearlite formation appears to be associated with their carbide forming tendency.²⁹ The greater this tendency, the more potent is the element in retarding pearlite. As an example of the magnitude of this retardation, the effect of molybdenum will be cited: 1% of this element retards by more than a factor of 1,000 the time required for a perceptible amount of pearlite to be formed.¹⁸

A current explanation of this retarding effect to be found in the literature runs as follows.³⁰ The concentration of the alloying element is observed to be greater in the

carbide phase than in the ferrite phase. The formation of pearlite is therefore associated with a segregation of the alloying element. Since the diffusion coefficient of all alloying elements is considerably less than that of carbon, such segregation must necessarily retard the rate at which the pearlite nodule grows.

As previously stated, all the elements which are very effective in retarding the formation of pearlite, molybdenum, titanium, etc., have a considerably stronger affinity for cementite than for austenite, and also have at most only a slight preference for austenite over ferrite. Therefore the free energy liberated by the propagation of a pearlite nodule would be increased by the presence of these alloying elements even if they remained uniformly distributed. The circumstance that the free energy would be still further lowered if the alloying elements became segregated in no way necessitates that the propagation of pearlite be attended by such segregation. As discussed in the section on bainite, the reaction which takes place is not necessarily associated with the greatest liberation of free energy, but proceeds at the fastest rate. The above explanation of the retarding effect of certain alloying elements leaves unanswered the fundamental question as to why the propagation of pearlite should have to wait for the segregation of the alloying elements.

It is in fact doubtful if any segregation of alloying elements takes place in the immediate vicinity of the expanding surface of a ferrite-cementite nodule. Such segrega-

tion as is observed could well take place within the nodule during the completion of the pearlite formation.

Under certain conditions the pearlite consists of alternate lamellae of ferrite and of a special alloy carbide which has a different structure from cementite.^{30,31} The growth of such a pearlite nodule must necessarily be accompanied by a segregation of the alloying element, and so proceeds very slowly. The question still remains unanswered, however, as to why in such cases ferrite-cementite nodules do not grow at their customary rate.

Any phase transformation involves both nucleation and growth. From the above discussion the fruitlessness is apparent of attempting to seek in growth an interpretation of the retarding effect of strong carbide forming elements upon pearlite formation. One is therefore led to seek for this interpretation in the phenomenon of nucleation.

Nucleation of pearlite always takes place at the grain boundaries unless the parent austenite has been imperfectly homogenized. This preference of nuclei for surfaces finds a ready interpretation in the fact that, as already explained in the section on nucleation, the formation of a nucleus entails the formation of an interface, and as a consequence the free energy of the nucleus must exceed a certain critical value before it becomes stable and is able to grow. As has been pointed out, this critical free energy is less when the nucleus forms at a boundary than when it

forms in the interior of a grain.

The same argument which has been used to show why nucleation is more prevalent at the boundary between two grains than in the interior of a grain, may be extended to demonstrate that nucleation is still more frequent along an edge common to three grains. A further extension may be used to demonstrate that nucleation is most frequent at corners common to four grains, and that the more acute the corner of any one grain the quicker will a nucleus be generated therein.

In any solid solution when the binding between a solute and a solvent atom is less than between two solvent atoms, the solute atoms will tend to congregate wherever the lattice is most disorganized. The situation is analogous to that of liquid solutions, in which the concentration of *certain* solute atoms is greater near the surfaces than in the interior. One therefore anticipates that the concentration of alloying elements in austenite will be greatest at those places which are potential nucleation sites, and the more effective are the sites for nucleation, the greater will be the concentration of alloying elements. If now the concentration of a strong carbide forming element is sufficiently large, the carbide nucleus which forms will not be cementite but a special carbide with a lattice structure different from that of cementite. The growth of the carbide grain resulting from such a nucleus will be slow, since it will be dependent upon diffusion of the alloying element. The growth will be

sufficient, however, completely to eliminate the original site as a potential nucleation site for cementite. The first additions of strong carbide forming elements therefore eliminate the sites which are most effective in nucleating cementite, and therefore retard slightly the initiation of pearlite growth. Further additions will lead to the elimination of the next most effective nucleation sites, retarding still more the initiation of pearlite growth.

B. Bainite and Martensite.

All alloying elements, save for the single exception of cobalt, both hinder the formation of bainite and lower the initial temperature, A_r'' , for the formation of martensite, and also have at least a normal influence in retarding pearlite formation. The observation that the order of alloying elements arranged according to effectiveness in retarding the bainite reaction is the same order with respect to the lowering of the martensite transformation temperature*, indicates that these two effects are closely related. In the martensite reaction nucleation is apparently nearly instantaneous,³² the initial transformation temperature not changing, within experimental error, in the range of cooling rates from 100 to 4000° C/sec. It therefore

*Private communication, J. H. Hollomon.

appears that the influence of alloying elements upon both the bainite and martensite reaction is not connected in any way with nucleation, as in the case of pearlite, but rather with a change in the equilibrium temperature of the two reactions.

As previously pointed out, the transformation from austenite to bainite and to martensite in pure iron-carbon steel is accompanied by no change in carbon distribution. Since the diffusion of alloying elements is even slower than that of carbon, it may safely be assumed that they also suffer no diffusion during the above two transformations. This assumption allows a ready calculation of the change in transformation temperature induced by these elements.

Let C_j be the ratio of the number of lattice atoms of type j to the total number of lattice atoms, $\Delta G_j^{\gamma \rightarrow \alpha}$ the change in atomic free energy when one mole of atoms of type j are transferred from the gamma to the alpha phase. The ratio of carbon to total number of lattice atoms will be denoted by C_c . Then the change in free energy associated with a transformation of one mole of lattice atoms and C moles of carbon from the austenite to the ferrite phase is given by the following equation

$$\Delta G = \Delta G_{Fe}^{\gamma \rightarrow \alpha} + \sum^{\prime} (\Delta G_j^{\gamma \rightarrow \alpha} - \Delta G_{Fe}^{\gamma \rightarrow \alpha}) C_j + \Delta G_c^{\gamma \rightarrow \alpha} C_c + \Phi \quad (26)$$

where the primed summation refers to all lattice type atoms

other than iron. In the case of the bainite reaction ϕ has a value lying between zero and $-(RT \ln 3) C_0$, in the martensite reaction it has the value of 357 cal/mole.

The influence of the alloying elements may most conveniently be expressed in terms of a horizontal shift of the transformation temperature vs. carbon content curve. From Equation (26) it may be seen that this shift is a linear function of the concentrations of the alloying elements, and therefore that the shifts are additive. This additive effect of different alloying elements has recently been suggested by Payson and Savage³³ from their ~~imperial~~ ^{empirical} data. The effect of a particular alloying element of type j with the atomic concentrations C_j is to shift to the left the transformation temperature vs. carbon concentration curve by the amount

$$\Delta C_c = \left\{ (\Delta G_j^{\gamma \rightarrow \alpha} - \Delta G_{Fe}^{\gamma \rightarrow \alpha}) / \Delta G_c^{\gamma \rightarrow \alpha} \right\} C_j \quad (27)$$

In the derivation of this equation, the last term in Equation (26) has been assumed to be a constant. This assumption introduces a slight approximation in the case of bainite.

It may be seen from Equation (27) that the larger the quantity $\Delta G_j^{\gamma \rightarrow \alpha}$, the greater the influence of the alloying element upon the bainite and the martensite transformation. At present the only method of evaluating the ΔG_j 's is through their influence¹ upon the iron-alloy equilibrium diagram. In such diagrams the equilibrium relations are usually

between austenite and nonmagnetic ferrite. It is to be expected that the atomic free energy change $\Delta G_j^{\gamma \rightarrow \alpha}$ will be greater below the Curie temperature than above, with the possible exception of cobalt which increases the Curie temperature at small concentrations. It is to be expected nevertheless that the order of the alloying elements should be the same when arranged according to the magnitude of their influence upon the bainite and the martensite transformation as when arranged according to their $\Delta G_j^{\gamma \rightarrow \alpha}$'s as measured at higher temperatures. The following table shows that this is in fact the case.

T A B L E I

Correlation of Effectiveness of Elements in Suppressing Bainite Reaction with Thermodynamical Quantities.

| Order of effectiveness* in suppressing bainite | C | N | Mn | Ni | Cu |
|---|-------|-------|------|------|------|
| $\Delta G^{\gamma \rightarrow \alpha}$ (cal/mole) | 9,600 | 3,000 | 2400 | 1600 | 1280 |

As previously mentioned, cobalt behaves in an anomalous manner. It actually hastens the bainite reaction, and raises the A_r'' temperature. An interpretation of this anomaly may be found from an inspection of the iron-cobalt equilibrium diagram. In this the gamma-delta boundary rises with increasing carbon content, while the gamma-alpha boundary is nearly horizontal. Such behavior is evidence that from 1400° to 900° C, $\Delta G_{Co}^{\gamma \rightarrow \alpha}$ changes from a positive quantity to zero. By extrapolation one surmises that at the

*Private communication, J. H. Hollomon.

lower temperatures at which bainite and martensite form, $\Delta G_{C_0}^{\beta \rightarrow \alpha}$ is a negative quantity.

IV. TIME-TEMPERATURE TRANSFORMATION CURVES

In this country the standard method of studying the decomposition of austenite is to quench the specimens from the austenitizing temperature to a lower temperature T , to hold at that temperature for a time t , and to then quench to room temperature. From an examination of the final specimens certain information may be gained as to the nature of the transformation which took place at the temperature T during the time t . The data so obtained is usually utilized to construct a diagram of the type represented in Figure 12, called the time-temperature-transformation (T-T-T) diagram. This diagram will be discussed in the light of the preceding portions of this report. The present discussion serves in part as a review of the salient features of this report.

The T-T-T diagram of Figure 12 consists of three sets of curves, each set corresponding to a distinct transformation product. Two sets consist of "C" curves, the other set of horizontal lines. This figure is idealized in that each set of curves is completely separated from the other two sets. The uppermost two sets are completely separated only in high alloy steel, such as in ^{high speed} tool steels. In plain carbon steels they are interpenetrating, the noses of the two sets nearly coinciding. In most steels the lower

two sets of curves are separated to some extent, but never completely so. Wherever two sets of curves interpenetrate, it is not possible to simply superimpose the two sets. In such cases not only does one reaction affect, either retarding or accelerating, the growth of the second reaction product, but the two reaction products may become indistinguishable.

None of the reaction products represent complete equilibrium at the temperature of formation. In the first reaction product, pearlite, complete equilibrium is attained only with respect to carbon. Here the carbide phase and ferrite occur as alternate lamellae, the lamellae growing edgewise into the parent austenite. The second reaction product, bainite, forms by grain growth from nuclei of ferrite of the same composition as the parent austenite. During the grain growth some carbon diffuses out of the ferrite grains into the surrounding austenite matrix. The higher the temperature of formation, the freer the ferrite is of supersaturated carbon. The third reaction product, martensite, forms by some sort of lattice shear which is homogeneous over macroscopic regions of the parent grains. This shear occurs so rapidly that there is no time for a change in composition. The only segregation of constituents that can occur in the martensite is that which may occur during self tempering after it has been formed.

In pearlite, and only in pearlite, may successive "C" curves be obtained essentially by a horizontal shift to the right of prior "C" curves. This essential parallelism of

the pearlite curves means that the ratio of the times required to come to two different completions is independent of temperature. Thus ten times as long may be required to come to 90% completion as to come to 10% completion. Only slightly below the eutectoid temperature are the curves no longer essentially parallel. Such non-parallelism occurs because in this temperature range the time required for growth is limited not only by the rate of growth of the pearlite nodules, but also by their nucleation rate.

The velocity with which a pearlite nodule advances is proportional to the diffusion coefficient of the carbon atoms, to the difference in the carbon concentration in the austenite just ahead of the advancing pearlite and cementite nodules, and is inversely proportional to the interlamellar spacing. This difference in carbon concentration is directly proportional, the interlamellar spacing is inversely proportional, to the amount of undercooling. When these various factors are properly considered, theoretical curves are obtained for the pearlite transformation which are nearly identical with the observed, except for a slight horizontal shift.

Only in the case of a eutectoid steel is pearlite the initial decomposition product of austenite. If the carbon concentration is greater than the eutectoid, a carbide first precipitates. If the carbon concentration is less than the eutectoid, free ferrite first forms. The critical temperatures which limits the range in which these products form

are interpreted by Figure 13.

In contrast to pearlite formation, bainite formation requires no diffusion of carbon. While the rate of growth of a pearlite nodule is proportional to the square of the amount of undercooling for temperatures just under the critical, the rate of growth of a bainite grain is independent of amount of undercooling for temperatures close to the critical temperature for bainite formation. The upper portion of the initial "C" curve for bainite is therefore essentially horizontal. While the growth of a bainite grain does not require carbon diffusion, nevertheless at the higher temperatures of formation carbon diffusion does occur, diffusion out of the growing bainite grain into the surrounding austenite matrix. Such diffusion finally stops the growth of a bainite grain by either one of two methods. The enrichment of the austenite in carbon tends to lower the transformation temperature of austenite to bainite, which tendency would eventually stop the growth of all grains. On the other hand, the enrichment of the austenite in carbon immediately surrounding the bainite grain may give rise to a cementite film, which film would prevent further growth. However the cessation of growth of bainite grains occur, it results in all the upper halves of the bainite isotherm transformation curves being horizontal. While, as previously mentioned, bainite grain growth is not dependent upon carbon diffusion, it does require the transfer of iron atoms from equilibrium positions on the austenite side of an inter-

face to new equilibrium position on the bainite side of the interface. The rate of such transfer will decrease with decreasing temperatures in the same manner, except less slowly, than does the rate of carbon diffusion. This decrease of rate of transfer of iron atoms with decreasing temperature results in the lower portions of the bainite isotherm transformation curves being of the same shape as for pearlite.

Freshly formed untempered martensite and bainite have essentially the same structure, namely ferrite supersaturated with carbon. The tetragonality of the martensite, in contrast to the cubic structure of bainite and of ferrite, is due to the circumstance that in the formation of martensite from austenite the carbon atoms are left in certain preferred interstitial positions. These preferred positions produce a strain with tetragonal symmetry, all the axes of the preferred positions being parallel. The essential difference, from the thermodynamical standpoint, of freshly formed martensite and freshly formed bainite lies in the elastic strains introduced during the formation of the former phase. These elastic strains require additional free energy for their formation, which additional free energy can be obtained only by a lowering of the transformation temperature for the austenite \rightarrow martensite reaction below that for the austenite \rightarrow bainite reaction. The residual strains introduced by the first martensite which forms renders it still

more difficult, i.e., requires more free energy and therefore a lower temperature for the formation of further martensite. The martensite reaction does not therefore proceed isothermally, a continual lowering of the temperatures being required for a continuance of the transformation. This circumstance leads to the isotransformation curves for martensite being horizontal lines. The vertical positions of the three sets of curves are determined primarily by the equilibrium relations. These relations are given in Figure 11 for plain carbon steels. Thus the upper boundary of the pearlite "C" curves is the eutectoid temperature. This temperature is raised by strong carbide forming elements such as molybdenum, tungsten, chromium, and is lowered most strongly by manganese and nickel. According to the theory developed in this paper, the upper temperature of the bainite "C" curves should be within the shaded region of Figure 11 for plain carbon steels, while the temperature for the initiation of martensite is given by the lowermost of the curves in this figure. Theory and experiment are in complete agreement for the case of martensite, while in the case of bainite the experimental data is inconclusive.

The horizontal positions of the two sets of "C" curves are sensitive to slight additions of alloying elements. The pearlite "C" curves are especially sensitive to strong carbide forming elements. These elements retard the formation of pearlite by covering up, with their own carbides, the

sites which are effective in the nucleation of cementite. Other elements, such as manganese and nickel, move all the "C" curves to the right through their effect in lowering the critical temperature for the formation of pearlite and of bainite. A lowering of the upper halves of the "C" curves must necessarily result in a shift of their noses to the right.

APPENDIX A

In this appendix that free energy is computed which is liberated within the interface itself as it advances. For the purposes of this computation we shall assume the solute concentration to be constant on both sides of the boundary.

As a unit area of the boundary advances a distance δX , the change in free energy δG may be written as

$$\delta G = \delta G_a - T \delta S_p \quad , \quad (a-1)$$

when δG_a is the change in atomic free energy, δS_p the change in positional entropy. Upon using the notation of section IC, we obtain

$$\delta G_a = \left\{ -\Delta G + (C_2 - C_1) (G_1 - G_2) \right\} \delta X \quad (a-2)$$

Further, upon using the methods in reference 1, one obtains

$$\delta S_p = \left\{ k(C_1 - C_2) - k(C_2 - C_1) \ln(\beta_2 C_1 / \beta_1 C_2) \right\} \delta X \quad (a-3)$$

Upon combining equations (a-1) - (a-3), and upon using equation (3)

$$\delta G = -\Delta G - kT(C_1 - C_2) \quad . \quad (a-4)$$

In order for δG to be less than or equal to zero, it is necessary that

$$(C_2 - C_1) \leq \Delta G / kT \quad ,$$

a relation which was used in the text.

APPENDIX B

In this appendix an analysis is made of the critical size and of the critical free energy of a nucleus.

The free energy liberated by the formation of a unit volume of the new phase will be denoted by G_v , the energy required to form a unit area of interface between the new and old phase will be denoted by G_s . The increase in free energy associated with the formation of a nucleus of the new phase is therefore

$$\Delta G = -VG_v + SG_s, \quad (b-1)$$

where V and S represent the volume and surface area of the nucleus, respectively. When the nucleus is completely surrounded by the old phase, its surface area, and therefore its free energy, is a minimum for a given volume when it is spherical. Such a nucleus may hence be regarded as spherical. Its critical radius is such as will make its free energy a maximum. From equation (b-1) this critical radius is found to be

$$R_c = 2G_s/G_v. \quad (b-2)$$

Substitution of equation (b-2) into equation (b-1) gives for the critical free energy

$$\Delta G_c = (16\pi/3) G_s^3/G_v^2 \quad (b-3)$$

As an example of the above equations, the case of a

cementite nucleus will be considered. Upon taking the energy per unit area of interface between cementite and austenite to be the same as between cementite and ferrite, one obtains, from equation (16), that G_s is equal to 6.8×10^{-5} cal./cm². Further, upon taking the heat of solution of cementite in austenite as 5,300 cal/mole¹, one obtains that for a eutectoid steel 100°C below the eutectoid temperature the free energy G_v to be 23 cal/cm³. Substitution of these quantities into equation (b-3) gives for the critical radius and for the critical free energy of a cementite nucleus of a eutectoid steel at 623° C,

$$R_c = 0.6 \times 10^{-5} \text{ cm.}$$

and

$$G_c = 1.0 \times 10^{-14} \text{ cal.,}$$

respectively.

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FIGURE 1.

Method of determining carbon concentration in austenite just ahead of an advancing ferrite or cementite grain.

FIGURE 2.

Variation of carbon concentration on two sides of advancing phase boundaries. (Examples of hypoeutectoid and hypereutectoid steels of Figure 1.)

FIGURE 3.

Schematic illustration of variation of equilibrium relations with curvature of interface surface.

FIGURE 4.

Illustration of mechanism of spheroidization of plate at the initial temperatures of formation.

FIGURE 5.

Illustration of advancing pearlite nodule.

FIGURE 6.

Variation of interlamellar spacing with temperature, plotted according to the theoretical equation (13). Straight line has a slope of -1 . (Data for eutectoid steel A of Reference 11.)

FIGURE 7.

Variation of interlamellar spacing with temperature, plotted according to method of Mehl. Same data as plotted in Figure 6.

FIGURE 8.

Carbon concentration in austenite ahead of advancing

pearlite nodule, drawn for 700° C after concept of Hultgren.¹⁵

FIGURE 9.

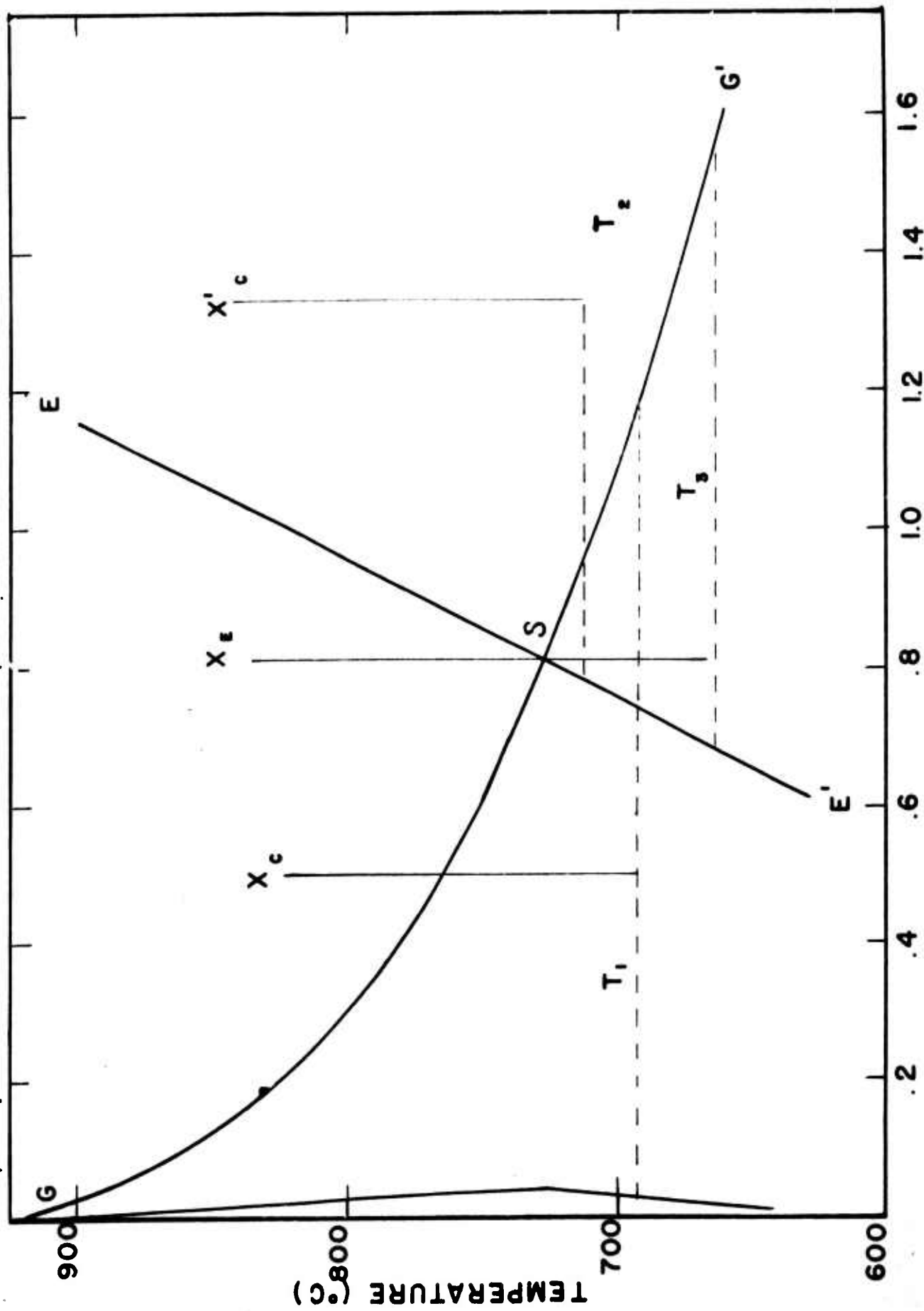
Pearlite "C" curve for infinite rate of boundary nucleation, drawn according to theoretical equation (18).

FIGURE 10.

Thermal diffusion coefficient of carbon in austenite, after data of Wells and Mehl.¹⁶

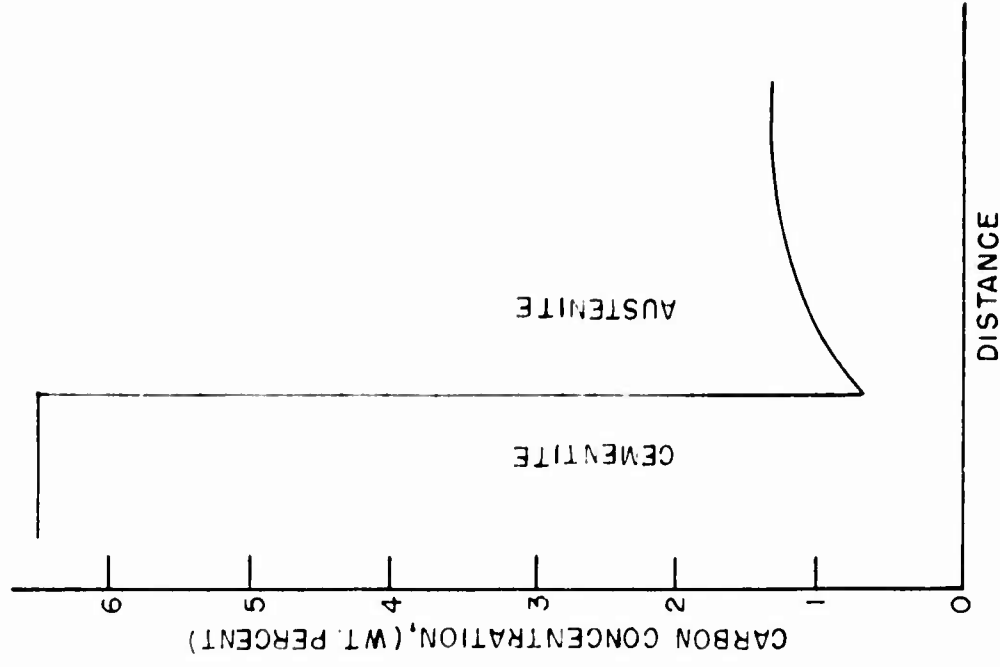
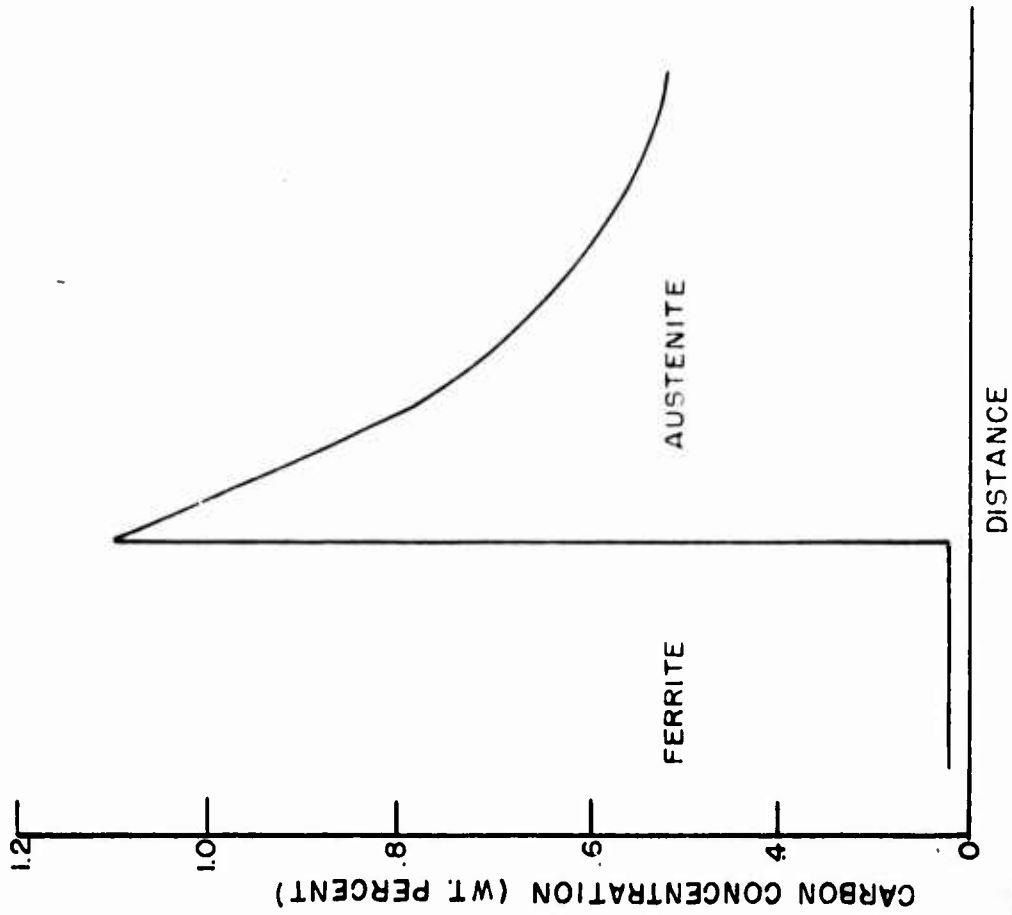
FIGURE 11.

Equilibrium relations in the iron-carbon system. The equilibrium relations between ferrite, austenite and cementite are as derived in Reference 1.

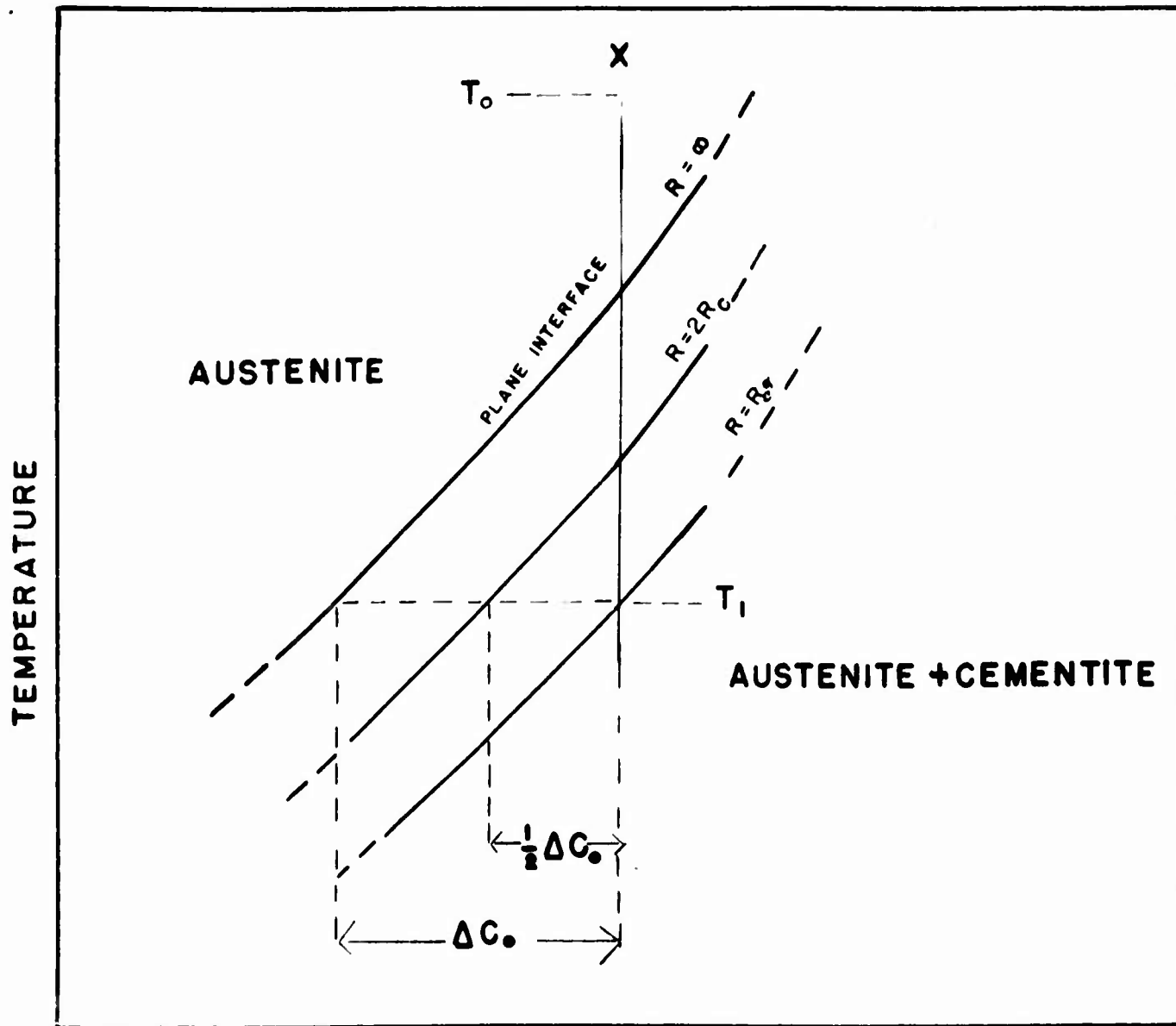


CARBON CONCENTRATION (WT.%)
 METHOD OF DETERMINING CARBON CONCENTRATION
 IN AUSTENITE JUST AHEAD OF AN ADVANCING FERRITE OR CEMENTITE GRAIN

FIG. 1



VARIATION OF CARBON CONCENTRATION ON TWO SIDES OF ADVANCING PHASE BOUNDARIES (EXAMPLES OF HYPOEUTECTOID & HYPEREUTECTOID STEELS OF FIG.1)
 FIG. 2



CARBON CONCENTRATION
 SCHEMATIC ILLUSTRATION OF VARIATION OF EQUILIBRIUM
 RELATIONS WITH CURVATURE OF INTERFACE SURFACE.

FIG. 3

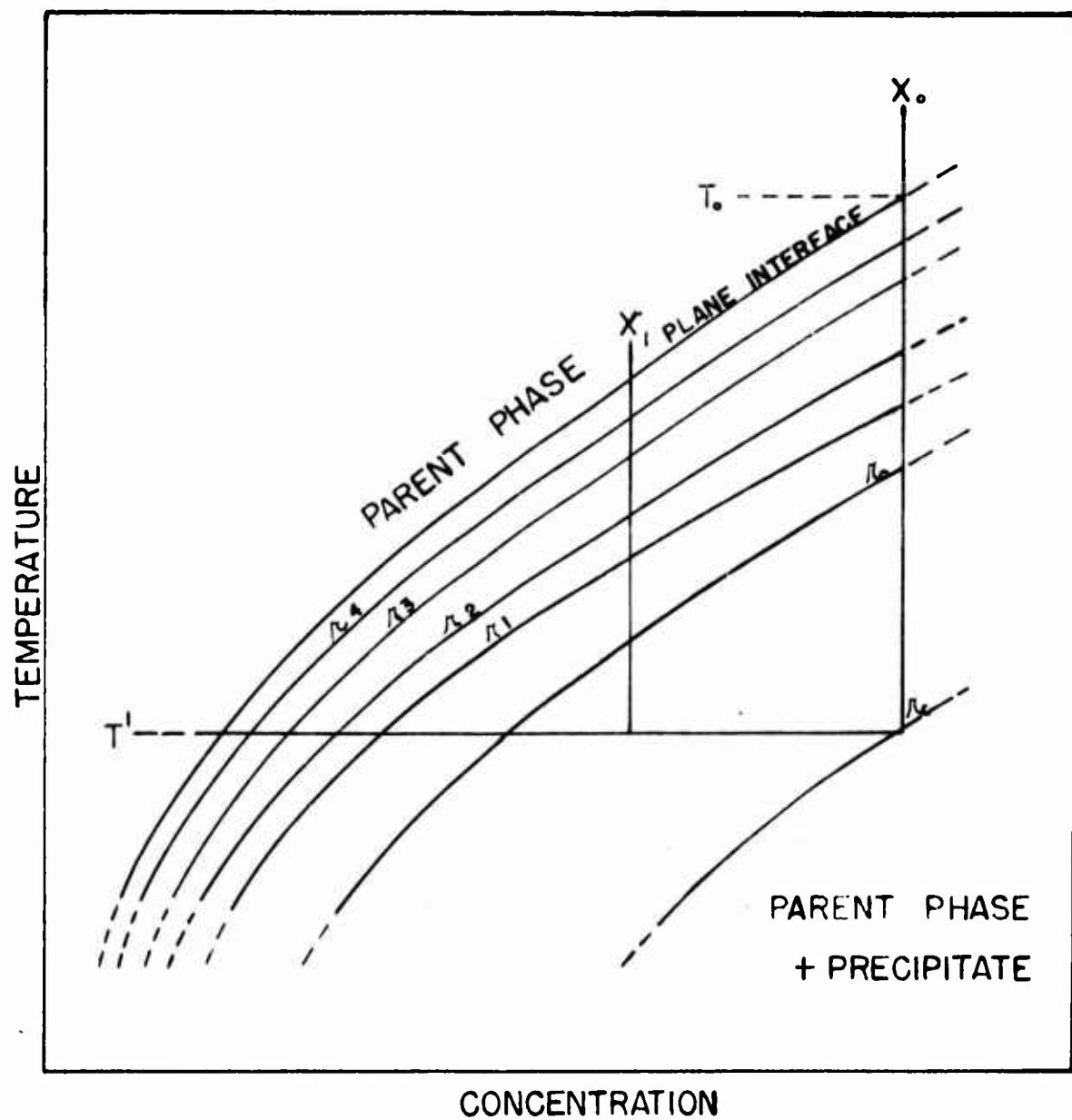


ILLUSTRATION OF MECHANISM OF SPHEROIDIZATION OF PLATE AT THE INITIAL TEMPERATURE OF FORMATION

FIGURE 4

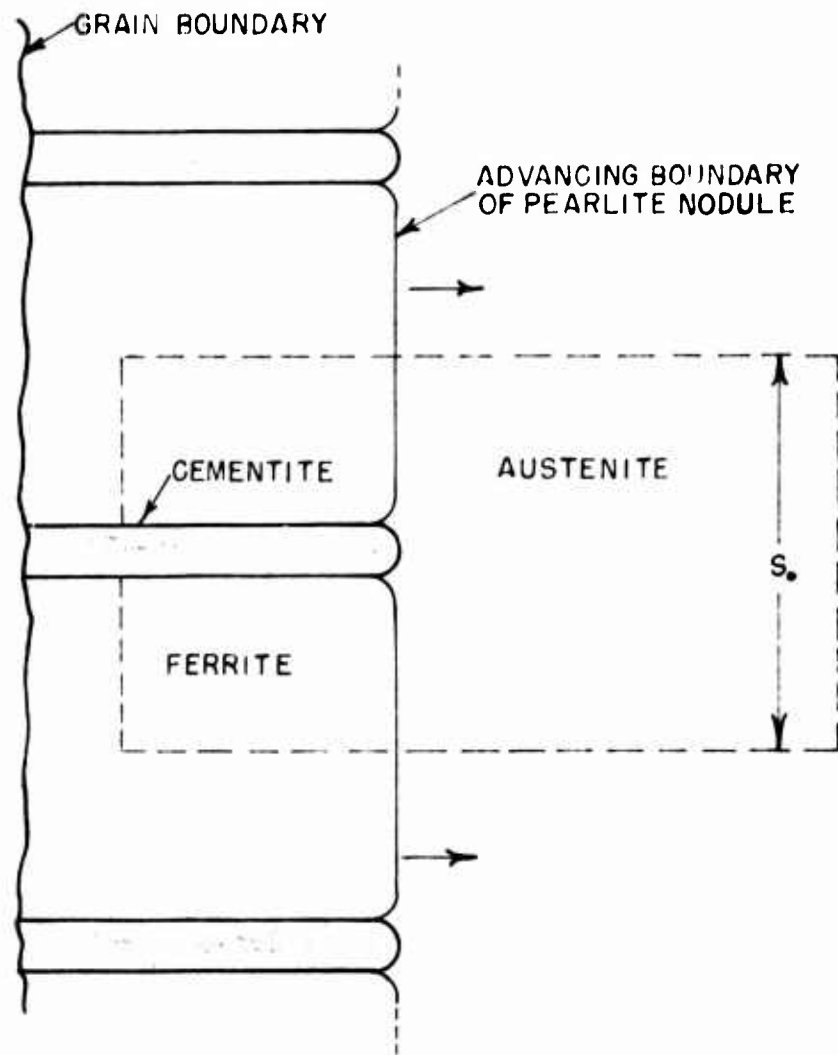
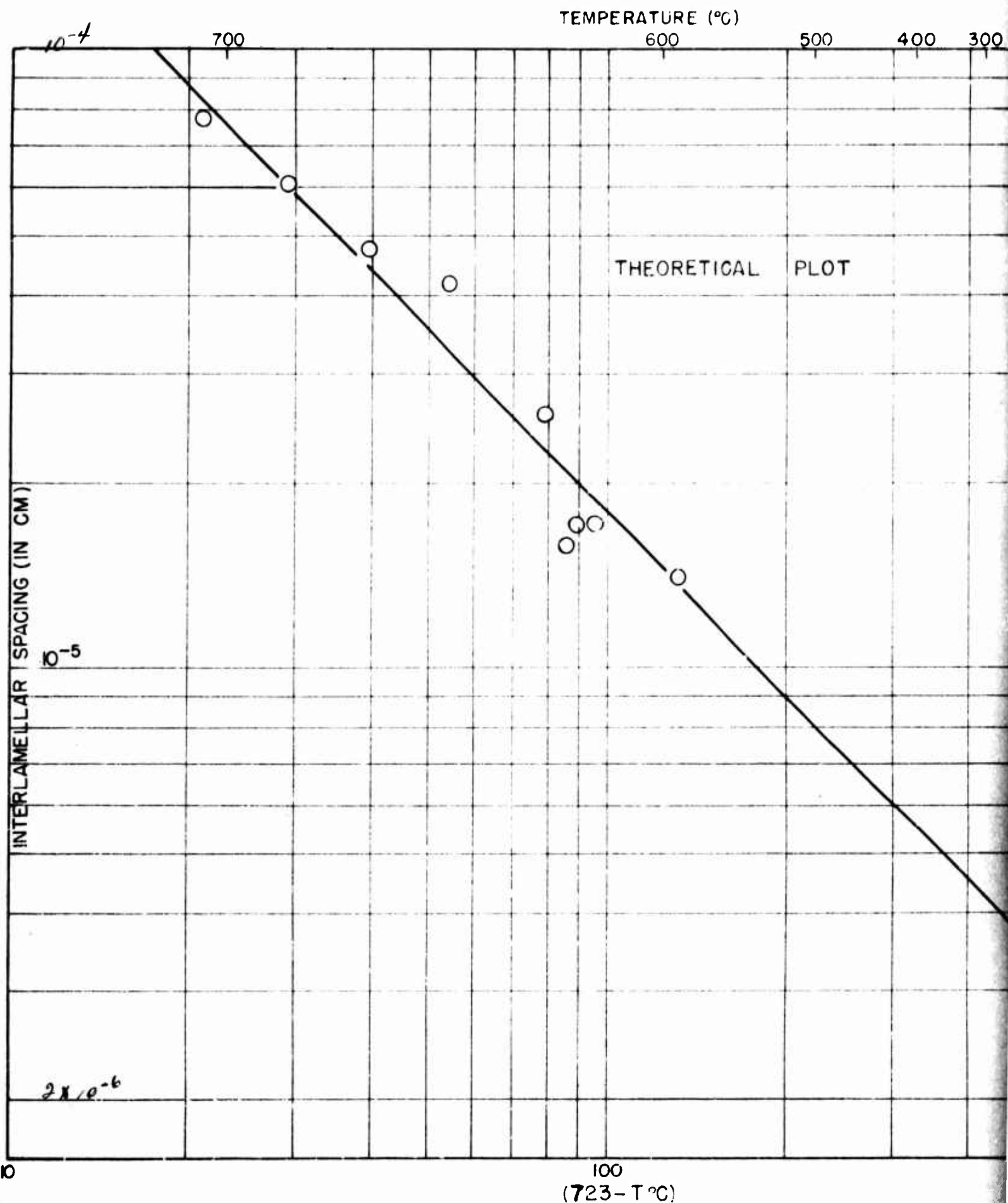
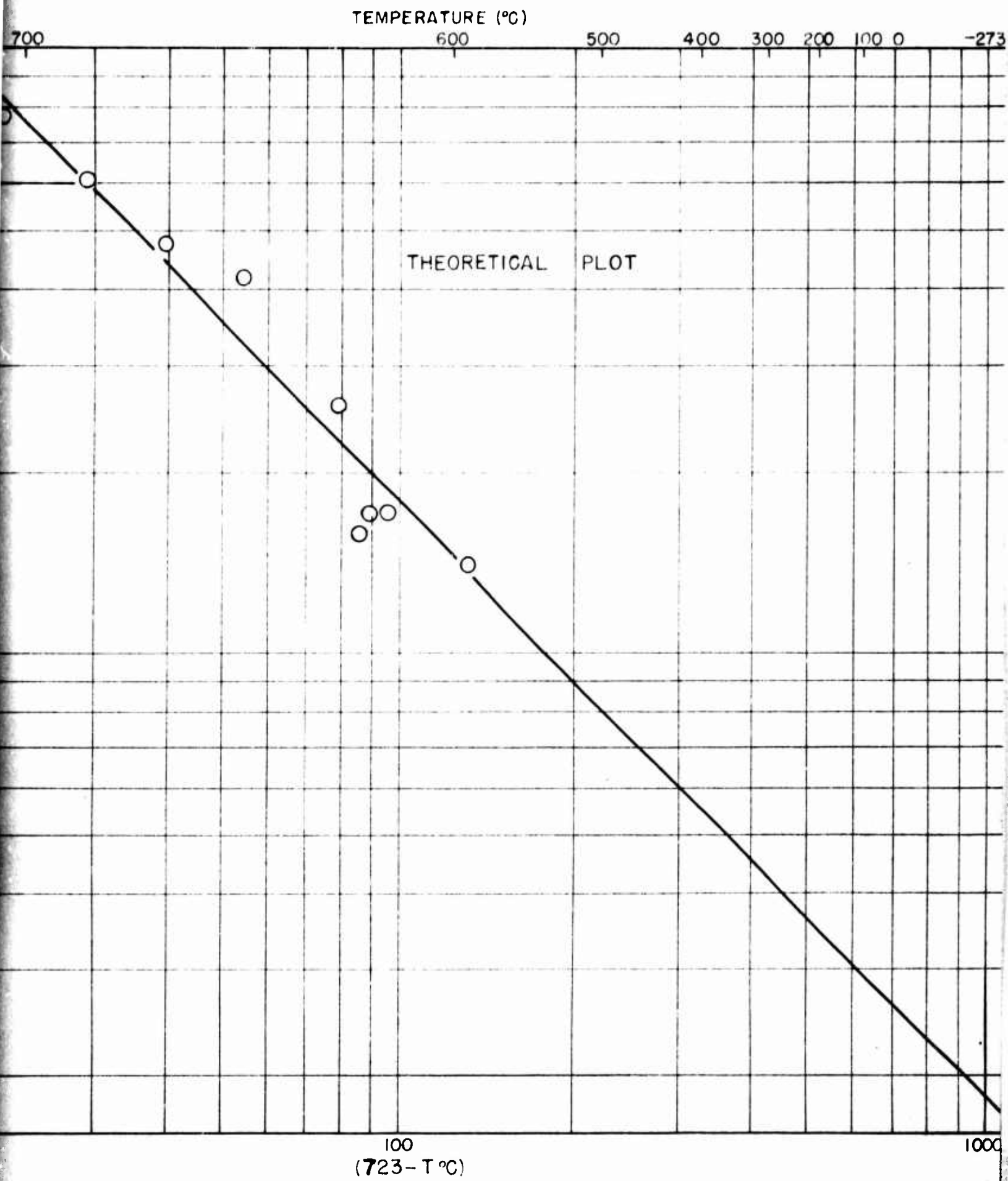


ILLUSTRATION OF ADVANCING PEARLITE NODULE

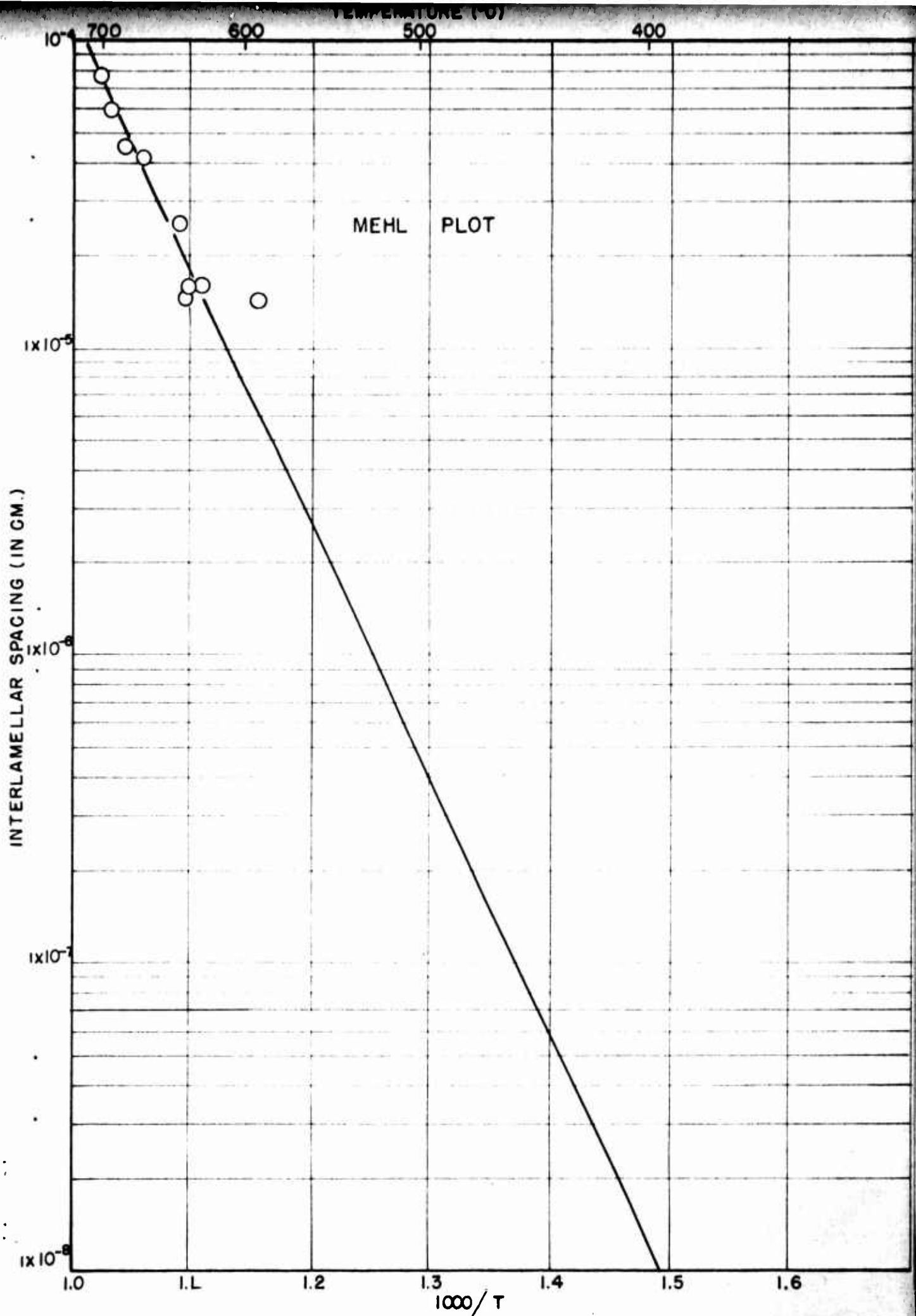
FIG. 5



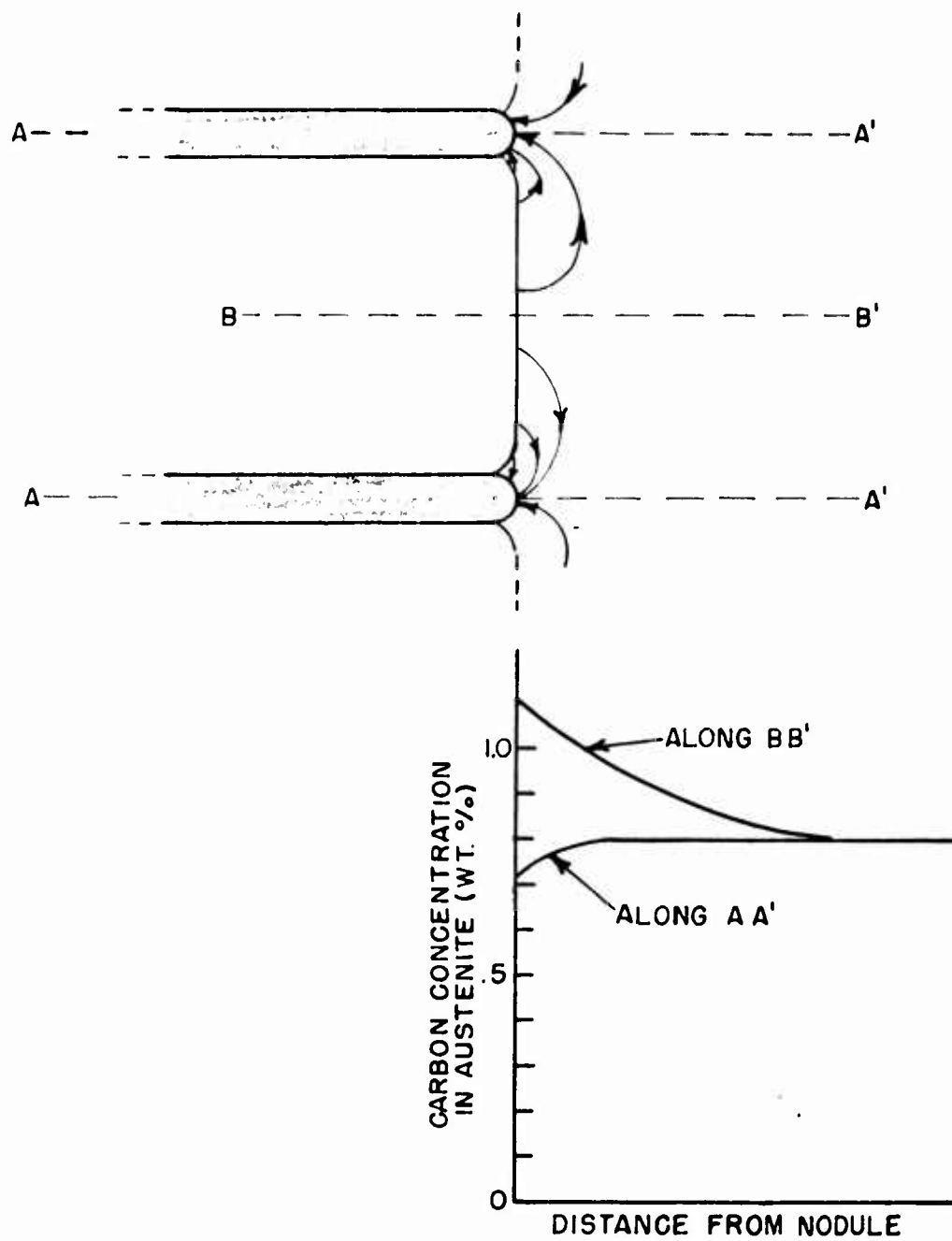
VARIATION OF INTERLAMELLAR SPACING WITH TEMPERATURE, PLOTTED ACCORDING TO THE THEORETICAL STRAIGHT LINE HAS SLOPE OF -1. DATA FOR EUTECTOID STEEL A OF REF. ●11. FIG. 6



LAMELLAR SPACING WITH TEMPERATURE, PLOTTED ACCORDING TO THE THEORETICAL EQUATION (13). STRAIGHT LINE HAS SLOPE OF -1. DATA FOR EUTECTOID STEEL A OF REF. 11.
 FIG. 6

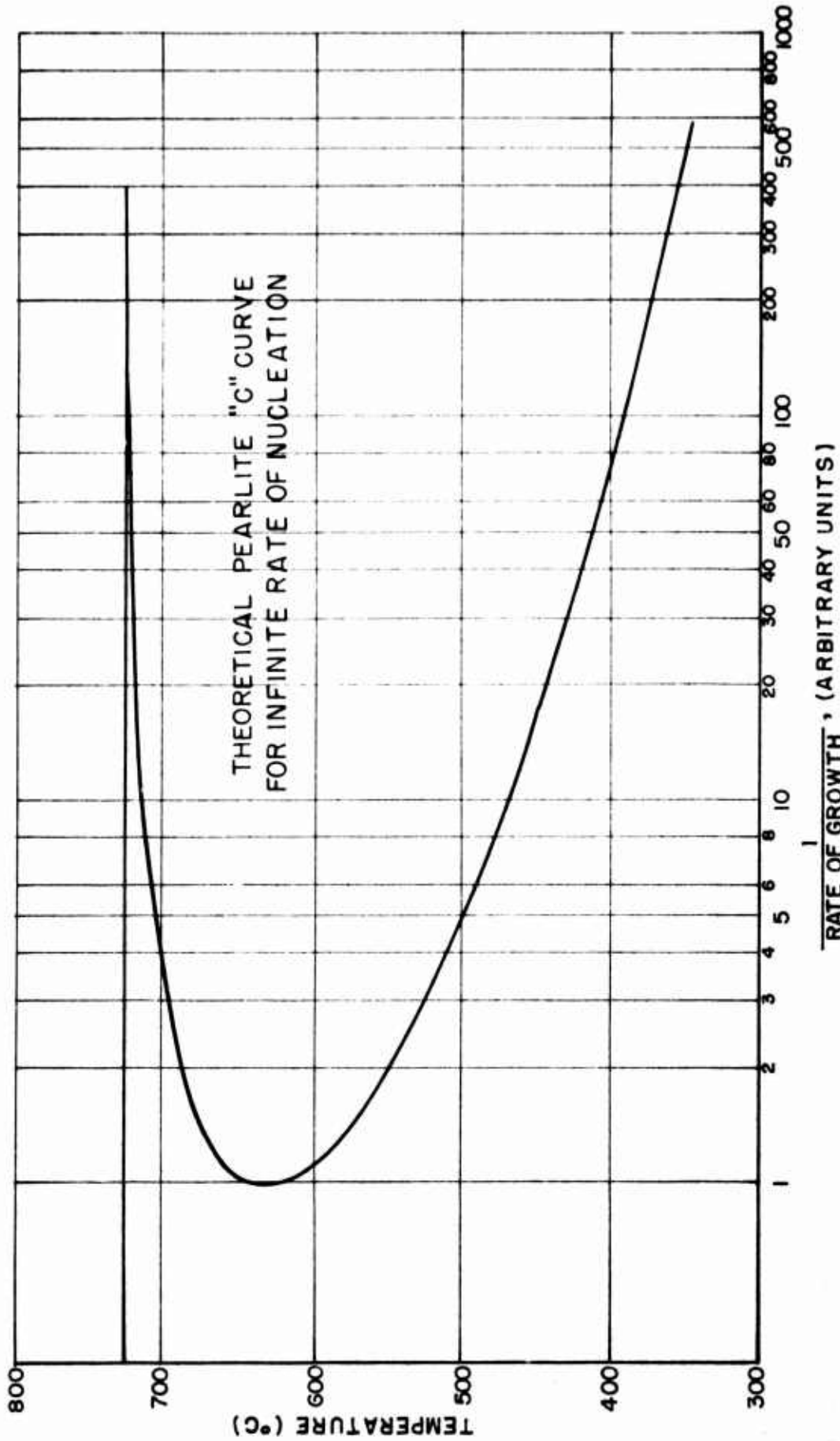


VARIATION OF INTERLAMELLAR SPACING WITH TEMPERATURE, PLOTTED ACCORDING TO METHOD OF MEHL. SAME DATA AS PLOTTED IN FIG. 6

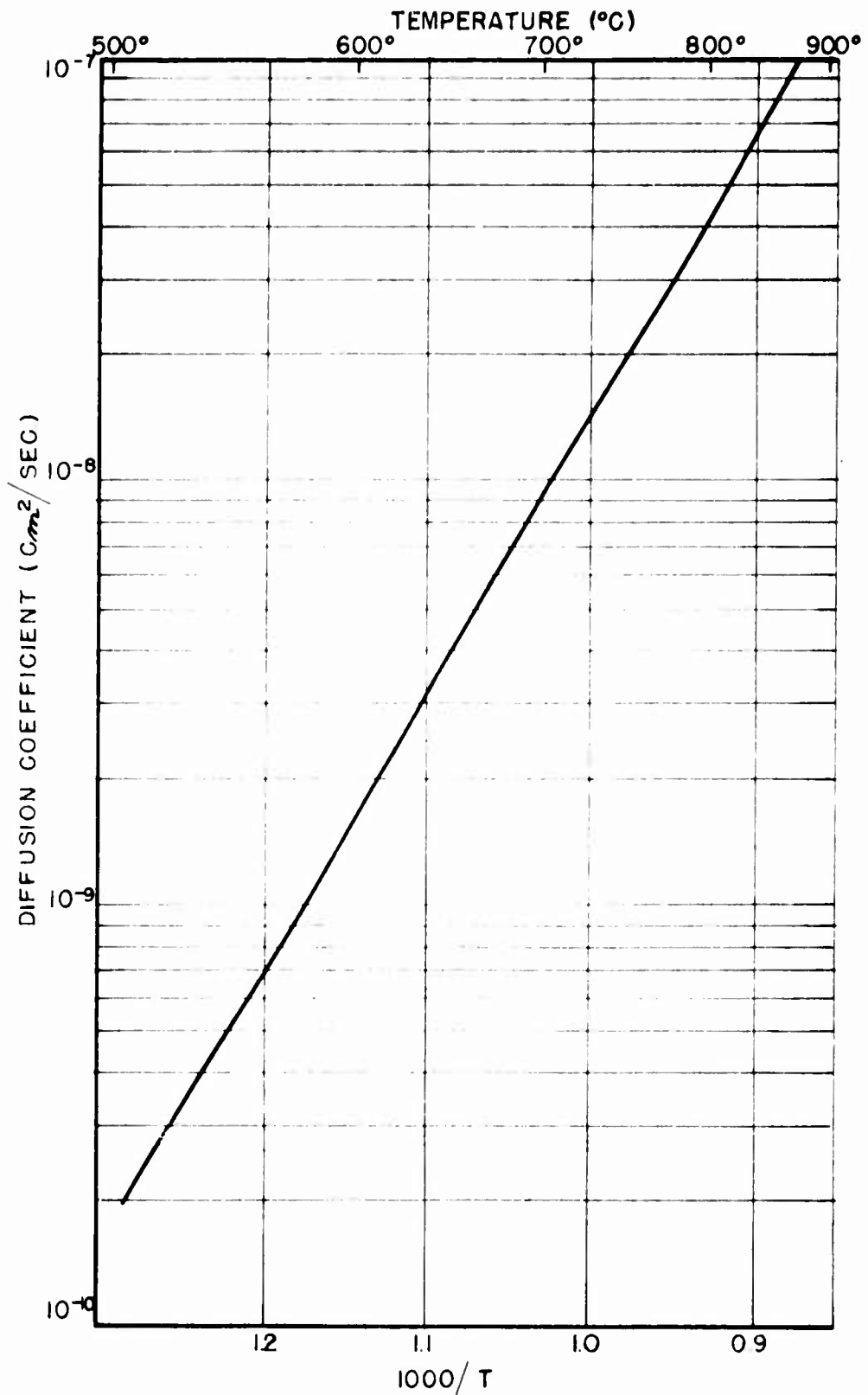


CARBON CONCENTRATION IN AUSTENITE AHEAD OF ADVANCING PEARLITE NODULE, DRAWN FOR 700 °C AFTER CONCEPT OF HULTGREN

FIG. 8

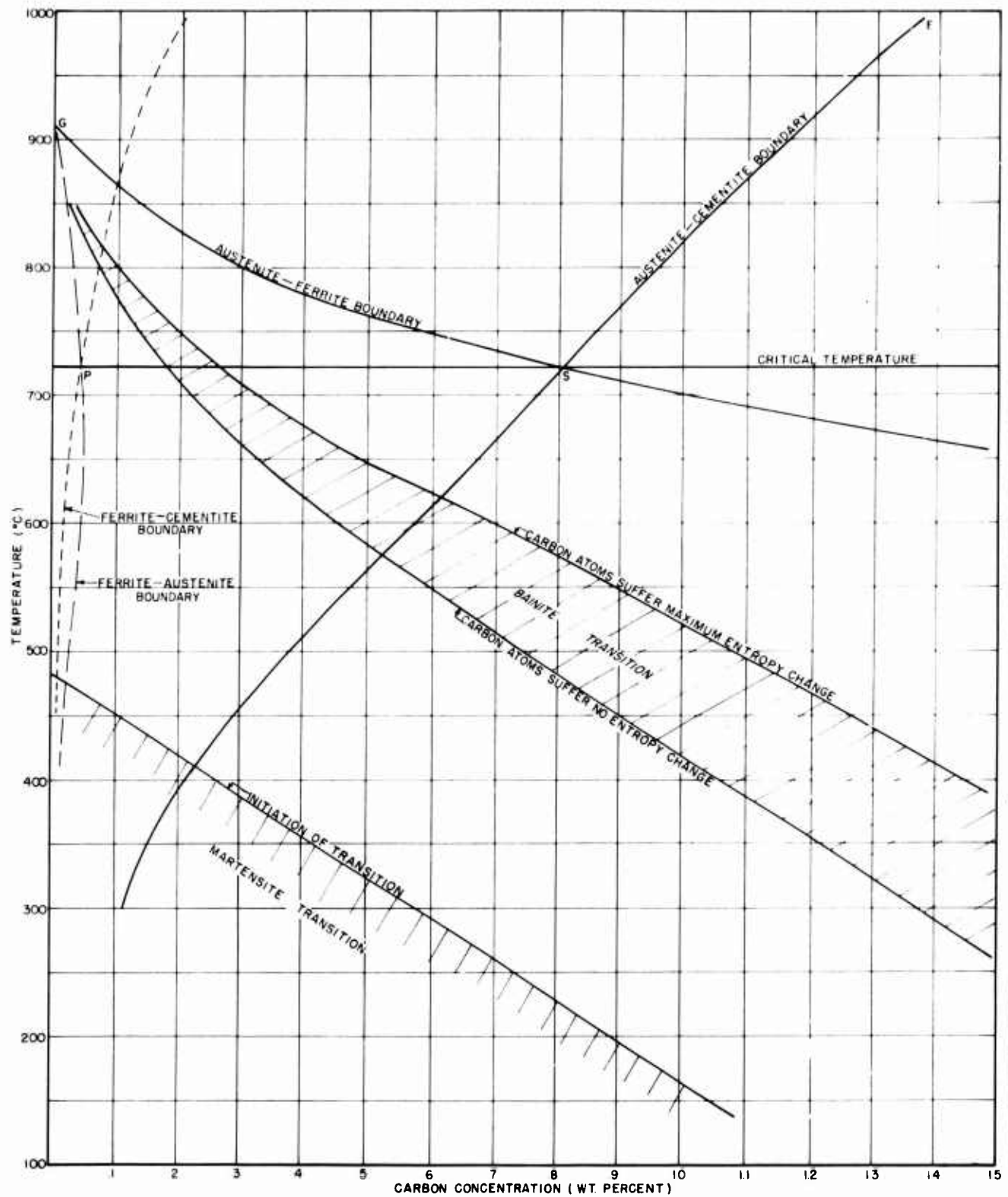


PEARLITE "C" CURVE FOR INFINITE RATE OF BOUNDARY
NUCLEATION, DRAWN ACCORDING TO THEORETICAL EQUATION (18)
FIG. 9



THERMAL DIFFUSION COEFFICIENT OF
 CARBON IN AUSTENITE, AFTER DATA OF
 WELLS AND MEHL¹⁶

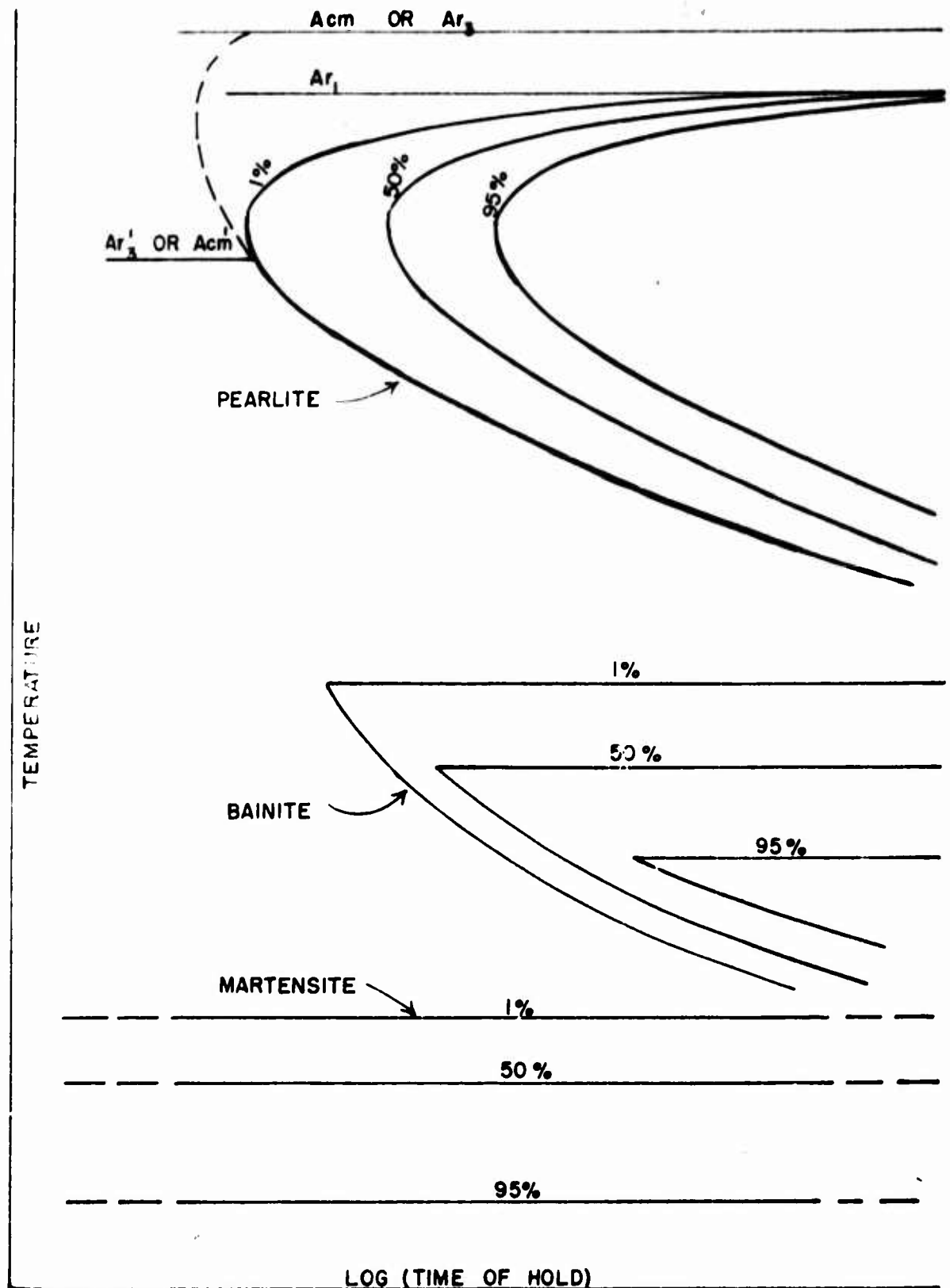
FIG. 10



EQUILIBRIUM RELATIONS IN THE IRON-CARBON SYSTEM. THE EQUILIBRIUM RELATIONS BETWEEN FERRITE, AUSTENITE & CEMENTITE ARE AS DERIVED IN REF. 1*

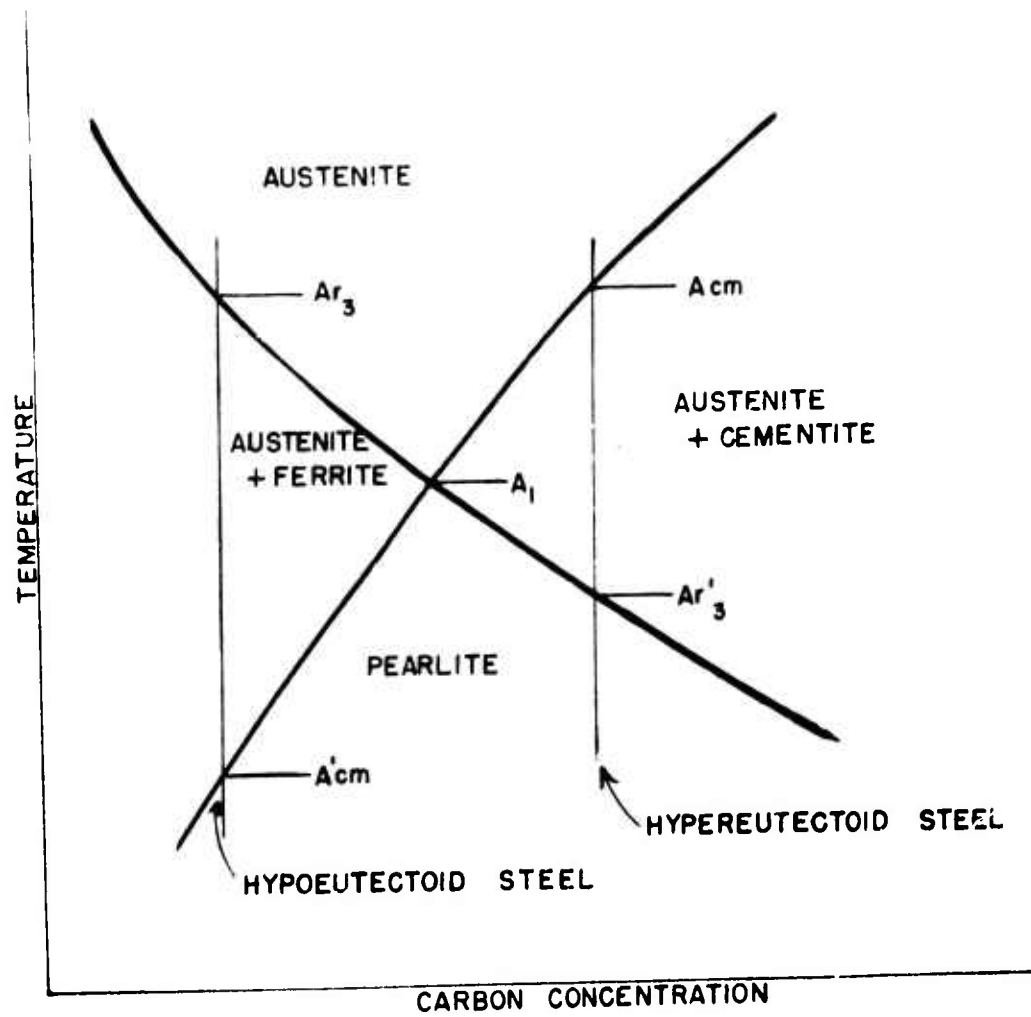
FIG. 11

WTN, 639-7216



IDEALIZED TIME - TEMPERATURE - TRANSFORMATION DIAGRAM

FIGURE 12



INTERPRETATION OF CRITICAL TEMPERATURES
IN FIGURE 12.

FIGURE 13



A. BAINITE PLATE PREVENTED FROM FURTHER GROWTH BY SURROUNDING FILM OF CEMENTITE.



B. PRECIPITATION OF CEMENTITE AS PLATES WITHIN BAINITE AREA.

FIGURE 14

EXAMPLES OF WAYS IN WHICH CEMENTITE MAY PRECIPITATE OUT OF BAINITE GRAINS. A5E STEEL 4140 WATER QUENCHED IN 3/4" ROUNDS. X2500

(THROUGH COURTESY OF MISS MARY A. NORTON)