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Author
Dairiki, O.

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O. Dairiki
(M.S. Thesis)

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SYNTHESIS OF S-SHAPED TEMPERATURE-TIME-TRANSFORMATION DIAGRAMS

Osamu Dairiki
MS Thesis

Materials and Molecular Research Division, Lawrence Berkeley Laboratory and Department of Materials Science and Mineral Engineering, University of California, Berkeley, CA 94720

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SYNTHESIS OF S-SHAPED TEMPERATURE-TIME-TRANSFORMATION DIAGRAMS

Osamu Diariki

M.S. Materials Science and Mineral Engineering Dept.

Chairman of Committee

ABSTRACT

Although the kinetics of isothermal transformation of steel have been studied by many researchers, it seems that there are few empirical models that can reproduce Temperature-Time-Transformation (T.T.T.) diagrams. Among these models, none seem to have both a sound physical background and wide applicability. Some make use of adjustable parameters which have no clear physical meaning, and others are restricted to fitting the C-shaped curves of plain carbon steels.

It is the purpose of the present investigation to construct a kinetic model of decomposition of austenite which is capable of reproducing both C-shaped and S-shaped T.T.T. diagrams of ternary steels using only a combination of physical parameters. In the model, two types of transformations, the pearlitic and bainitic, are treated simultaneously. Elastic energy and concentration "spike" effects due to local equilibrium conditions at the interface are taken into account. The model can reproduce not only T.T.T. diagrams, but also calculate the partitioning coefficient of the alloying element between ferrite and carbide. The model was applied to Fe-0.80%C, Fe-0.81%C-1.41%Cr and Fe-0.81%C-1.41%Ni
steels, and proved to be capable of reproducing both C-shaped and S-shaped T.T.T. curves, showing that C-shaped curves are particular cases of S-shaped curves.
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I. INTRODUCTION

Heat treatments are of utmost importance in improving the properties of metals and alloys. Although heat treatments have been done for thousands of years, it was not until this century that fundamental research on these processes began. The most important work in this field should be the introduction of isothermal transformation by Bain and co-workers. Because the temperature is fixed, the interpretation of isothermal transformation is much simpler than that under continuous cooling. The temperature-time-transformation (T.T.T.) diagram is the most significant fruit of that method. Although most heat treatments are done under continuous cooling, T.T.T. diagrams are of central importance. Because continuous-cooling-transformation (C.C.T.) diagrams, which directly correspond to the treatment, are dependent upon various factors such as the cooling facility, coolant, size and shape of the specimen, each treatment of a particular product requires a specific diagram. On the other hand, a T.T.T. diagram is independent of those factors except for grain size. Moreover, a T.T.T. diagram can be translated into C.C.T. diagrams. Hence, most work on kinetics in heat treatment has been done along T.T.T. diagrams.

Many researchers have tried to model the kinetics of phase transformation, especially that in decomposition of austenite. It seems that there are two types of approaches: One is the thorough research of every detail of phenomena related to the kinetics. Aaronson and his co-workers are doing this type of effort and obtaining excellent results. The reality is, however, so complicated that so far they are unable to synthesize T.T.T. diagrams properly. The second approach
is the empirical approach done by Kirkaldy, Bhadeshia, Tamura, and so forth. They were able to reproduce some T.T.T. diagrams successfully. Although the method has its origin in Russel's incubation time, which has a physical background, it is essentially a curve-fitting method. Thus, when extending its application to various systems, the method inevitably uses some parameters which do not have sound background.

The present investigation is intended to provide an intermediate method. In other words, the simplest model, with all parameters having proper physical meaning, is to be developed. The model is to be capable of reproducing not only C-shaped T.T.T. diagrams, but also S-shaped ones. In order to avoid too much complexity, the model is to be restricted to eutectoid decomposition of binary or ternary steels.

II. MODEL

A. Basic Assumptions

In the present study, binary and ternary steels of near eutectoid composition are treated. For simplicity, the concentration of carbon in the ferrite phase is assumed to be 0.02 percent weight, and the carbide phase is of cementite type, i.e., \((\text{Fe}\cdot\text{M})_3\text{C}\). Since the transformation is eutectoid, the concentrations of carbon in two product phases are known; once the composition of the parent phase is fixed, composition of all three phases is fixed with only one additional parameter. As the final parameter, a partitioning coefficient \(p\) of the following definition is chosen:
\[ p = \frac{Z^\theta_M}{Z^\alpha_M}, \]  
(II.1)

with
\[ Z^\phi_i = \frac{c^\phi_i}{1 - c^\phi}, \]  
(II.2)

where \( c^\phi_i \) is mole fraction of the \( i \)-th element in phase \( \phi \) \((\phi = \alpha: \) ferrite, \( \theta: \) carbide), \( M \) representing the third elements. In the above definition, \( Z \) is a concentration variable appropriate for the present research, whereas \( C \) stands for the ordinary mole fraction. This situation is illustrated in Figure 1. The composition of each phase is given as follows:

**Austenite:** \( Z^\gamma_{Fe}, Z^\gamma_C, Z^\gamma_M \),

**Ferrite:** \( Z^\alpha_{Fe} = 1 - Z^\alpha_M \),
\[
Z^\alpha_C = 0.001,  
Z^\alpha_M = \frac{Z^\gamma_M}{1 - \beta + \beta p},
\]

**Cementite:** \( Z^\theta_{Fe} = 1 - Z^\theta_M \),
\[
Z^\theta_C = \frac{1}{3},  
Z^\theta_M = pZ^\alpha_M, \]  
(II.3)

where \( \beta \) is the ratio of cementite to decomposed austenite expressed in the number of metal atoms:
\[
\beta = \frac{Z^\gamma - Z^\alpha}{Z^\theta - Z^\alpha}. \]  
(II.4)
Two types of decompositions are considered. One is pearlite transformation and the other is bainite transformation. Both transformations are assumed to be controlled by diffusion. In the present research, it is assumed that substitutional elements diffuse only by the exchange of elements, i.e., the exchange of Fe and M. This assumption does not prohibit the vacancy mechanism of diffusion, but simply prohibits the net flux of vacancies. In front of the growing pearlite, a disordered austenite or "transition area" is assumed. In the area, the diffusivity of the substitutional elements is assumed to be much greater than that in the bulk. In bainite transformation, due to high coherency between bainite and the parent phase, increase of elastic energy is taken into account, while no transition area is assumed. In both cases, heterogeneous nucleation is assumed. Ferrite and cementite are considered to nucleate simultaneously and to grow cooperatively, as illustrated in Figure 2.

B. Rate of Transformation

A version of the Johnson-Mehl equation is applied.\textsuperscript{9,10}

\[ X = 1 - \exp(-X_e) \quad (II.5) \]

where \( X \) is the ratio of transformed phase, and \( X_e \) is the so-called extended volume fraction. We are indebted to Avrami\textsuperscript{11} for the concept of extended volume fraction. Although the concept was originally limited to homogeneous nucleation, it was extended to the heterogeneous case by Cahn.\textsuperscript{12} In the present research, two additional extensions are made. The first is "additivity" of the extended volume fraction. The
sum of two extended volume fractions, which correspond to two different types of product phase, replaces the original single extended volume fraction:

\[ x_e = x_e^P + x_e^B \]  \hspace{1cm} (II.6)

where \( x_e^P \) is extended volume fraction of pearlite, and \( x_e^B \) that of bainite.

The additivity holds under the following two conditions. One is that both types of transformation have a sufficient number of nucleation sites even after nucleation of the other; that is, nucleation sites of two types of transformations are independent from each other, or both types of transformations take place under steady-state nucleation. Umemoto, et al.\(^9\) showed that the ratios of both types of transformations are approximately proportional to the fourth power of holding time. According to Cahn,\(^{12}\) the fourth power law means "nucleation and growth" or steady-state nucleation. The other condition is that the probabilities of transformations, in the sense of extended volume fraction, are the same in all untransformed phases. This condition does not seem much more restrictive than the original assumption by Avrami,\(^{11}\) where only one type of transformation was considered.

The second extension is with regard to the partitioning of the third element between ferrite and carbide. The partitioning of the third element is the most critical factor in the decomposition of ternary steels. The partitioning coefficient defined by Eq. (II.1) is used in the calculation of both nucleation- and growth rate. Values of the partitioning coefficients are chosen so that they give the maximum
value to each rate, following the concept of "maximum transformation rate" of Zener.\(^{13}\) Two different partitioning coefficients are used for each type of transformation, because nucleation and growth are considered independent phenomena; that is, at the nucleation stage, nuclei do not care how they grow and the growing nuclei have no memories of their creation.

C. Nucleation Rate

A "duplex nucleus," illustrated in Figure 2, is treated according to classical nucleation theory\(^{14}\) as a single particle. The work of nucleation is

\[
W = \frac{K_2}{\Delta F^2}, \tag{II.7}
\]

where \(K_2\) is a parameter proportional to the cube of the effective surface energy, and \(\Delta F\) is the reduction of volume energy, or "driving force," per one mole of transformation. The probability to obtain the required products by diffusion is

\[
P_m = K_m \nu M, \tag{II.8}
\]

where \(M\) is a "global mobility" (which will be discussed later), \(\nu\) is an average atomic vibrational frequency, and \(K_m\) is some proportionality factor. Then the nucleation rate is

\[
I = K_1 TM \exp\left[-\frac{K_2}{(RT\Delta F^2)}\right], \tag{II.9}
\]

where \(K_1\) is a constant which is the product of the proportionality coefficient for Eq. (II.8) and density of nucleation sites. Finally,
the optimal rate of nucleation is obtained by maximizing with respect to the partitioning coefficient \( p \):

\[
I_M = \max_p \left\{ K_1 TM(p) \exp\left[ -\frac{K_2}{RT\Delta F^2(p)} \right] \right\} . \tag{II.10}
\]

D. Growth Rate

Duplex or cooperative growth of ferrite and cementite, which keeps the composition of austenite at its original value, is assumed. Applying the classic theory of diffusion controlled growth, one obtains, for the volume of a nucleus

\[
V = K_3 (Gt)^m , \tag{II.11}
\]

\[
G = \frac{J_C^p}{m_C} , \tag{II.12}
\]

where \( G \) is the "growth factor," \( t \) the holding time, \( m \) a shape exponent, \( J_C^p \) the partitioning flux of carbon, and \( m_C \) is the required partitioning of carbon from ferrite to carbide. The partitioning flux, \( J_C^p \) will be discussed later in Section II-H. In the present study, the shape exponent is fixed to be 3, which corresponds to the spherical growth of nuclei. However, nuclei are not actually spherical; they are spherical only in the sense of extended volume. In the above growth formula, the volume of the nucleus is neglected because of its extremely small size. Maximizing with respect to the partitioning coefficient, one obtains

\[
G_M = \max_p \left\{ \frac{J_C^p}{m_C} \right\} . \tag{II.13}
\]
E. Extended Volume Fraction

The extended volume fraction is calculated to be

\[ X_e = \int_0^t I_M V_M (t-\tau) \, d\tau \quad \text{(II.14)} \]

The above integral can be worked out with some assumptions on \( I_M \).

Since in the present treatment steady state nucleation is assumed, we find

\[ X_e = \frac{1}{4} K_3 I_M G_M^3 t^4 \quad \text{(II.15)} \]

F. Driving Force

The driving force for the transformation is calculated as the sum of Gibbs' free energy and that of elastic energy. Thus the driving force per one mole of decomposition is,

\[ \Delta F = (1-\beta)(g^\gamma-g^\alpha) + \beta(g^\gamma-g^\theta) - \Delta E \quad \text{(II.16)} \]

where \( g^\theta \) is Gibbs' free energy per one mole of \( \theta \) phase, \( \Delta E \) is the increase of elastic energy per one mole of transformation, and \( \beta \) is the ratio of cementite defined by Eq. (II.4). Changes in Gibbs' free energy are calculated from published thermodynamic data. For the Fe - C and Fe - C - Cr systems, a regular solution model by Sharma et al. is used. For the Fe - C - Ni system a sub-regular solution model by Ührenius is applied.
G. Spike Effect

If two phases are not at full equilibrium, at the interface, the composition of each phase is, in general, different from that in the bulk. Thus there appear gradients of concentration, or "spikes," as illustrated in Figure 3. The concept of local equilibrium\(^{17}\) is then applied to calculate the concentration at the interface. The local equilibrium condition requires continuity of the chemical potentials of each element at the interface,

\[
\phi_1 \frac{\mu_A^1}{\mu_A^1} = \phi_2 \frac{\mu_A^2}{\mu_A^2} ,
\]

where \(A\) is any element in the system, and \(\phi_1\) and \(\phi_2\) are the neighboring phases. The above conditions are necessary to avoid an infinite gradient of chemical potential which would cause infinite rate of transport. In the present study, since exchange of elements is the only way of diffusion allowed for substitutional elements, the local equilibrium conditions for those elements are replaced by

\[
\phi_1 \frac{\mu_A^1}{\mu_B} = \phi_2 \frac{\mu_A^2}{\mu_B} ,
\]

where \(A\) and \(B\) stand for substitutional elements. Thus, the condition between austenite and ferrite are

\[
\mu_A^\alpha - \mu_M^\alpha = \mu_M^\gamma - \mu_M^\gamma ,
\]

\[
\mu_C^\alpha = \mu_C^\gamma .
\]

In cementite, however, as it is a stoichiometric compound of fixed carbon concentration, the chemical potential of the separate elements cannot be defined. Hence the condition between austenite and cementite is
According to Hillert,\textsuperscript{17} the width of the spike is
\begin{equation}
W_S = \frac{D}{v},
\end{equation}
where $D$ is the diffusion coefficient of the element, and $v$ is velocity of the moving interface. For metal elements, considering bulk diffusion, the width turns out to be less than atomic dimension.\textsuperscript{17}

Thus, spikes of metal elements are allowed only inside the disordered area immediately ahead of the interface, where those elements can diffuse much faster than in the bulk. According to the present model, a spike is allowed in the transition area in front of the advancing pearlite. Because of the extremely high dependence of the chemical potential of carbon upon its concentration in both ferrite and cementite, only very small spikes in those phases can keep the continuity of the chemical potential at both ferrite-austenite and cementite-austenite interface. Therefore, the spike of carbon is neglected in the present research; that is, the second Eq. (II.19) is not applied in the actual calculation. Concentrations at the top of the spikes are calculated by Eqs. (II.19) and (II.20), using (sub-) regular solution models which are used in the calculation of the driving force. Moving spikes in the transition area in front of the growing pearlite require continuous diffusion of materials. Those diffusions consume some part of the driving force of the transformation and delay the process. This phenomenon will be treated in Sections II-H and II-I.
H. Diffusion

Diffusion responsible for the transformation is assumed to take place in the austenite region. In addition, substitutional elements, due to their high sensitivity to structure, tend to choose "quicker paths" in the disordered area. Thus, at the nucleation stage, diffusion of those elements is restricted to defects, such as grain boundaries and dislocations. In front of the growing pearlite, they diffuse in the transition area. In front of the bainite, however, lack of the transition area force the elements to diffuse in bulk austenite. Figure 4 illustrates various diffusion paths.

For each element two kinds of flux are defined. One is the "partitioning flux" required to obtain the average composition of ferrite and cementite. The other is the "spike flux" required to maintain the spikes (see Figure 5).

Materials to be carried by the partitioning flux during the decomposition are calculated from Eq. (II.3). For one mole of metal elements:

\[ m_C = 2\beta \left( \frac{1}{3} - Z_C^Y \right) , \]

\[ m_M = m_{Fe} = \frac{2\beta(p-1)(\beta-1)Z_M^Y}{1 - \beta - \beta p} . \]  

(II.22)

The intensity of flux is to be proportional to required material:

\[ J_i^D = K m_i , \]  

(II.23)

where \( K \) is a proportionality coefficient. Thus, the partitioning flux is
\[
J^D_C = 2K\beta \left( \frac{1}{3} - Z^\gamma_C \right),
\]
\[
J^D_M = -J^D_{Fe} = \frac{2K\beta(p-1)(\beta-1)Z^\gamma_M}{1 - \beta - \beta p}, \tag{II.24}
\]
where direction of flux is taken from ferrite to cementite. Spike flux at the interface is calculated by the height of the spikes.

\[
J^S_{C,\phi} = \frac{Z^\gamma_{C,\phi} - Z^\gamma_C}{Z^\phi_C - Z^\gamma_C} J^D_C,
\]
\[
J^S_{M,\phi} = -J^S_{Fe} = \frac{Z^\gamma_{M,\phi} - Z^\gamma_M}{Z^\phi_C - Z^\gamma_C} J^D_C, \tag{II.25}
\]
where \(Z^\gamma_{C,\phi}\) is the concentration of the element at the top of the spike in front of the \(\phi\) phase; other concentrations are values in the bulk.

In the present study, as explained in the preceding section, the spike flux of carbon is neglected;

\[
J^S_{C,\phi} = 0. \tag{II.26}
\]

The average intensity of spike flux will be required in the next section to calculate the "global mobility." Going away from the interface into the bulk, the spike flux decreases and its average length of diffusion is, as shown in Figure 5, about half the width of the spike. At high temperature, as two spikes interfere with each other, spikes saturate to a "straight construction" as illustrated in Figure 6. Thus the average length of spike flux is
where \( \lambda_p \) is the length of the path itself, and average intensity of the flux along a path is

\[
\overline{J_M^S} = \frac{J_M^{S,\alpha} \lambda_M^{S,\alpha} + J_M^{S,\theta} \lambda_M^{S,\theta}}{\lambda_p}.
\]  

Finally, taking the average over various paths, yields

\[
\overline{J_M^S} = \left( \frac{J_M^{S,\alpha} \lambda_M^{S,\alpha} + J_M^{S,\theta} \lambda_M^{S,\theta}}{\lambda_p} \right). 
\]

As shown by Eq. (II.21), where the diffusion coefficient \( D \) is the dominating term, \( W_s \) is a strongly increasing function of temperature. Thus, \( \lambda_M^S \)'s are also strong increasing functions of temperature saturating at some value given by the length of the path, \( \lambda_p \). Taking the average over paths with various lengths, the saturation makes \( \lambda_M^S \)'s much weaker functions of temperature. Thus the following approximation does not seem to cause serious error:

\[
\overline{J_M^S} = \sigma(J_M^{S,\alpha} + J_M^{S,\theta}),
\]

\[
\sigma = \sigma_1 - \sigma_2/T,
\]

where \( \sigma_1 \) and \( \sigma_2 \) are constants. The maximum value of 1/2 for \( \sigma \) is attained when the temperature is high enough to allow the "straight
construction" for every path, and a spike at either ferrite-austenite or cementite-austenite interface is negligible. Finally, the average flux of each element is

\[ J_C = J_C^P, \]

\[ J_M = -J_{Fe} = J_M^P + \sigma (J_M^{s, \alpha} + J_M^{s, \theta}) \]  \hspace{1cm} (II.31)

I. Mobility

In the calculation of mobility, for simplicity, one representative diffusion path for each element is treated. In these paths, both partitioning flux and spike flux are assumed to be uniform along the paths. This situation is illustrated in Figure 7.

The partitioning flux of carbon is chosen as "representative flux" because that is the only flux proportional to the rate of decomposition. "Global mobility," \( M \) is defined as

\[ J_C^P = M \cdot \Delta F \]  \hspace{1cm} (II.32)

For each element,

\[ J_i = -B_i C_i \Delta \psi_i \]  \hspace{1cm} (II.33)

where \( B_i \) is mobility, and \( \psi_i \) is the potential responsible for the flux. The potential \( \psi_i \) corresponds to the energy consumed by diffusion of one mole of \( i \)-th element per unit length. The potential is, so far, an unknown combination of elastic potential and chemical potentials of all elements. Units on \( M \) and \( \psi \) are adjusted so that finite differences rather than gradients may be used in Eqs. (II.32) and (II.33).
The energy consumed by diffusion of one mole of each element down the corresponding potential is

\[ e_i = \lambda_i \nabla \psi_i d_s \quad \text{(II.34)} \]

where \( \lambda_i \) is the length of the diffusion, \( d_s \) is a length along the diffusion path. If, for simplicity, \( \nabla \psi_i \) is assumed to be constant along a path, then

\[ \nabla \psi_i = \frac{-\Delta \psi_i}{\lambda_i} \quad \text{ (II.35)} \]

and

\[ e_i = \Delta \psi_i \quad \text{ (II.36)} \]

Thus, the energy consumed by one mole of partitioning flux is

\[ E_d = \frac{J_C}{J_C^{\text{p}}} m_C \Delta \psi_C + \frac{J_{Fe}}{J_{Fe}^{\text{p}}} m_{Fe} \Delta \psi_{Fe} + \frac{J_M}{J_M^{\text{p}}} m_M \Delta \psi_M \quad \text{ (II.37)} \]

Equating this to the driving force per one mole of metal elements:

\[ E_d = \frac{\Delta F}{1-c_c^\gamma} \quad \text{ (II.38)} \]

Inserting Eqs. (II.33) and (II.35) into (II.37) to eliminate the \( \Delta \psi \)'s and using Eqs. (II.23) and (II.38), Eq. (II.32) is solved for \( M \),

\[ M = \frac{1}{m_C(1-c_c^\gamma)} \left[ \left( \frac{J_C}{J_C^{\text{p}}} \right)^2 \frac{\lambda_C}{B_C C_C} + \left( \frac{J_{Fe}}{J_{Fe}^{\text{p}}} \right)^2 \frac{\lambda_{Fe}}{B_{Fe} c_{Fe}} + \left( \frac{J_M}{J_M^{\text{p}}} \right)^2 \frac{\lambda_M}{B_M c_M} \right]^{-1} \quad \text{ (II.39)} \]
Because diffusion of substitutional elements is allowed only by exchange of elements,

\[ \lambda_{\text{Fe}} = \lambda_M \quad \text{(II.40)} \]

For carbon, because of its high diffusivity, its path can stretch deep inside the austenite. When diffusion of metal elements is restricted in the disordered area, the diffusion path of carbon is, in average, much longer than those of metal elements. However, because of the small ability of longer paths to transport material, and the large uncertainty of diffusivity in the disordered area, it is simply assumed,

\[ \lambda_C = \lambda_M \quad \text{(II.41)} \]

For concentrations in Eq. (II.39), as averages, the values in original austenite are used:

\[ c_i = c^{\text{\gamma}}_i \quad \text{(II.42)} \]

So far, the detail of the potential, \( \psi_i \), is unknown. Thus, the value of the mobility, \( B_i \), is also unknown. However, if the potential is the chemical potential of the element, and the solution is dilute,\textsuperscript{18}

\[ D_i = D_{i_0} \exp(-Q_i/RT) = B_iRT \quad \text{(II.43)} \]

Taking advantage of Eq. (II.43), it is assumed that

\[ D_i = D_{i_0} \exp(-Q_i/RT) = K_4B_iT \quad \text{(II.44)} \]

where \( K_4 \) is a proportionality coefficient. Thus, the final form of the global mobility is
Values of diffusion coefficients are taken from published data,19,20,21 and for "high-mobility paths," Q's are replaced by $\frac{2}{3} Q$.

J. Summary of Formulae

\[ M = \frac{1}{K_{\phi}^{\phi} C_{\phi}^{\phi} C_{\phi}^{\phi}} \left[ \frac{1}{D_{C}Z_{C}} + \left( \frac{J_{M}^{p} + \sigma(J_{M}^{s,\alpha} + J_{M}^{s,\theta})}{J_{C}^{p}} \right)^{2} \left( \frac{1}{B_{\phi}^{Z_{\phi}}} + \frac{1}{B_{M}^{Z_{M}}} \right) \right]. \] (II.45)

\[ X = 1 - \exp(-X_{e}^{P} - X_{e}^{B}) \]

\[ X_{e} = K_{1}^{\phi} I_{M}^{\phi}(G_{M}^{\phi})^{3} t^{4} \quad (\phi = P \text{ or } B) \]

\[ K_{1}^{\phi} = \frac{K_{1}^{\phi} K_{3}^{\phi} K_{4}^{l} C_{\phi}^{l} m_{C}}{4} \]

\[ I_{M}^{\phi} = \frac{I_{M}^{\phi}}{K_{1}^{\phi} K_{4}^{l} C_{\phi}^{l} m_{C}} = T \cdot \max\{M'(p) \exp[-K_{2}^{\phi}/[RT\Delta F^{2}(p)]]\} \]

\[ G_{M}^{\phi} = \frac{G_{M}^{\phi}}{K_{4}^{l} C_{\phi}^{l}} = \max\{M'(p) \Delta F(p)\} \]

\[ M'(p) = K_{4}^{l} C_{\phi}^{l} m_{C} M(p) = \frac{1}{T} \left[ \frac{1}{D_{C}Z_{C}} + \left( \frac{J_{M}^{p} + \sigma(J_{M}^{s,\alpha} + J_{M}^{s,\theta})}{J_{C}^{p}} \right)^{2} \left( \frac{1}{B_{\phi}^{Z_{\phi}}} + \frac{1}{B_{M}^{Z_{M}}} \right) \right]^{-1} \]

\[ \sigma = \sigma_{1} - \sigma_{2}/T \quad (\text{II.46}) \]

\[ J_{M}^{s,\alpha}, J_{M}^{s,\theta} \text{ and } \Delta F \text{ are calculated by solution models.} \]
III. CALCULATION

A. System and Programs

A micro-computer combined with a digital plotter was used to calculate and plot T.T.T. diagrams. The system is illustrated schematically in Figure 8.

Three programs were created to obtain T.T.T. diagrams for Fe-C, Fe-C-Cr and Fe-C-Ni steels. For the latter two systems, the programs are identical to each other except for the diffusion coefficient of the third element and the thermodynamic model used to calculate the driving force and the spike. The program for plain carbon steel is much simpler, because it is free from the partitioning of the third element and the spike. This program requests $K_1$, $K_2$ and $\Delta E$ for both pearlite and bainite transformation. For ternary systems, programs request composition of steels in addition to those parameters required by the program for plain carbon steel. The elastic energy $\Delta E$ is always set to zero for the pearlite transformation. Those programs calculate the aging times required for 1% and 99% transformation at each temperature from 650°K to 1100°K with increments of 25°K. For ternary systems, during the calculation, partitioning coefficients at both nucleation and growth stages are calculated. Finally, the computer drives the plotter, interpolating five points between each pair of calculated points, and draws T.T.T. diagrams and partitioning curves. Figure 9 is the flow chart of the programs.
B. Calculation Procedure

First, the T.T.T. diagram of eutectoid plain carbon steel (Fe-0.80%C) was calculated. $K^P_2$ was chosen so as to get the pearlite nose and the proper temperature. $K^B_2$ was fixed equal to $K^P_2$, because of the lack of information about surface energy. Then $K^{B'}_1/K^{P'}_1$ and $\Delta E^B$ were chosen so that two small C-curves corresponding to individual pearlite and bainite transformations combined to produce a large C-curve. The bainite curve appeared at about 800°C. At that point, the T.T.T. diagram of the plain carbon steel was fixed with an arbitrary unit of time. In the calculation of curves for the Fe-0.81%C-1.41%Cr system, for which Chance and Ridley obtained experimental curves, $K^{B'}_1/K^{P'}_1$ was kept at its original value used for the plain carbon steel. $K^B_2$'s for both pearlite and bainite were kept equal to each other, chosen to get the pearlite nose at the experimentally-determined temperature. At the same time, $\Delta E^B$ was adjusted so as to fit the bay to the experimental result. This $\Delta E^B$ was applied back into the calculation of the plain carbon steel. Then, absolute values of $K^{'1}_1$'s were fixed to fit the calculated curves horizontally to the experimental ones. Those $K^{'1}_1$'s were also applied to the plain carbon steel. $\sigma_1$ and $\sigma_2$ were chosen to fit the calculated partitioning coefficient at growth to the experimental data. Finally, T.T.T. diagrams of Fe-0.81%C-1.41%Ni steel were calculated. In that calculation, $K^{'1}_1$'s, $K^{'2}_2$'s, $\Delta E$'s, and $\sigma$ were kept as they were for the Fe-C-Cr system.

In order to check the effect of $\sigma$, some additional calculations were made.
IV. RESULTS AND DISCUSSION

The calculated results are shown in Figures 10 to 15, in which all start curves correspond to 1% transformation and end curves to 99% transformation. Parameters used in those calculations are shown in Table 1. Figure 10 shows the T.T.T. diagram of eutectoid plain carbon steel (Fe-0.80%C) with separated start curves corresponding to pearlite and bainite. The figure illustrates the construction of a large C-curve from two small C-curves. Figure 11-a is the calculated T.T.T. diagram of Fe-0.81%C-1.41%Cr with experimental data by Chance and Ridley. The calculated curves and experimental data fit, at least for pearlite, very well. Figure 11-b shows the calculated partitioning coefficient at nucleation. In Figure 11-c, the calculated partitioning coefficient at growth is compared with the experimental data, showing fairly good coincidence. Figures 12-a to 12-c illustrate the calculated results for Fe-0.81%C-1.41%Ni steel. This composition is the same as that of the preceding chromium steel, except for the change of the third element. In the present research, both the chromium steel and the nickel steel used are known to be nearly eutectoid. Using the same parameters as for the chromium steel, except for diffusion and thermodynamic data, the calculated T.T.T. diagram of the nickel steel in Figure 11-a shows C-curves instead of S-curves. The C-curves are typical of nickel steel. Figure 11-c shows, as expected, almost no partitioning of nickel between ferrite and carbide. The above results seem to prove the capability of the present model to reproduce both C-type and S-shaped T.T.T. diagrams, along with partitioning curves of the third elements.
In those three cases, the parameter $\sigma$, which represents the relative importance of the spike flux to the partitioning flux, was assumed to be given by Eq. (II.30), with $\sigma_1$ set to unity and $\sigma_2$ to 600. Since the above assumption was somewhat tentative, the effect of $\sigma$ was checked. Figures 13-a to 15-c show calculated results for the chromium steel (Fe-0.81%C-1.41%Cr). In these calculations, $\sigma$ was set constant while all other parameters were kept as in the previous calculation. These figures show that the T.T.T. diagram is not so sensitive to $\sigma$ as the partitioning coefficient at growth. Hence, it seems possible to fit both the T.T.T. diagram and the partitioning coefficient to the experimental data by choosing the proper function of $\sigma$ on temperature. However, because calculation of the partitioning coefficient is not the main interest of this research, precise study of $\sigma$ was left to future investigation.

Among the many parameters fixed in the calculation, absolute values of $K_1'$s are not meaningful until austenite grain size is given, because $K_1'$s are proportional to the density of nucleation site which is highly dependent upon the grain size. Only the rate, $K_1^{B'}/K_1^{P'}$ is important to give a shape of a T.T.T. diagram, while absolute values of $K_1'$s only shift the diagram horizontally.

The model in the present work is limited to near-eutectoid composition. It is, however, not difficult to obtain start curves of off-eutectoid systems. Because at the onset of transformation, composition change in the parent phase is negligible, taking into account only one product phase in the calculation of the driving force and the spike effect, the present model can be applied. Unfortunately, the model is
not capable of calculating curves corresponding to the arbitrary ratio of transformation of off-eutectoid cases. In order to calculate those curves, an additional model which takes care of composition change in the parent phase is to be developed.

V. CONCLUSION

A simple model has been developed to synthesize T.T.T. diagrams. Taking into account nucleation-and-growth theory and spike effect, the model can reproduce both C-shaped and S-shaped T.T.T. diagrams. The parameters used in the model are all combinations of physical parameters which can, at least in principle, be measured independently. C-shaped curves were shown to be particular cases of S-shaped curves.
ACKNOWLEDGEMENTS

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REFERENCES

1. E. C. Bain, Functions of the Alloying Elements in Steel, ASM, Cleveland, 1939.


Table 1. Parameters

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<th>Figure</th>
<th>$K_{1}^{P}$</th>
<th>$K_{1}^{B}$</th>
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<th>$\Delta E^{B}$</th>
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Diffusion Coefficient

C; $D_0 = 0.036 \times 10^{-4} \text{ m}^2/\text{s}$, $Q = 30600 \text{ cal/mole}$
Fe; $D_0 = 0.089 \times 10^{-4} \text{ m}^2/\text{s}$, $Q = 69600 \text{ cal/mole}$
Cr; $D_0 = 0.169 \times 10^{-4} \text{ m}^2/\text{s}$, $Q = 62980 \text{ cal/mole}$
Ni; $D_0 = 0.108 \times 10^{-4} \text{ m}^2/\text{s}$, $Q = 65150 \text{ cal/mole}$
FIGURE CAPTIONS

Fig. 1. Compositions of the parent phase and two-product phases, and the relation among them.

Fig. 2. Geometrical assumptions for the transformation.
   (a) Duplex nucleation
   (b) Cooperative growth

Fig. 3. Concentration "spike" due to local equilibrium. The highest spike appears at no-partition, local equilibrium case. No spike is necessary at full equilibrium case.

Fig. 4. Various diffusion paths of substitutional elements. (Carbon always diffuses in bulk austenite.)
   (a) At nucleation stage
   (b) In front of growing pearlite
   (c) In front of growing bainite

Fig. 5. Partitioning flux and spike flux.

Fig. 6. Construction of concentration spike.
   (a) "Straight construction" at high temperature
   (b) Separate spikes at low temperature

Fig. 7. Representative path and flux.

Fig. 8. Schematic illustration of the micro-computer system used in the present research.

Fig. 9. Flow charts of the programs for ternary steels. (For plain steel, maximization processes are by-passed.)
   (a) Main program
   (b) Functions
Fig. 10. Calculated T.T.T. diagram of Fe-0.80%C steel with two separated start curves.

Fig. 11. Calculated results of Fe-0.81%C-1.41%Cr steel.
   (a) T.T.T. diagram with experimental data
   (b) Partitioning coefficient at nucleation
   (c) Partitioning coefficient at growth with experimental data

Fig. 12. Calculated results of Fe-0.81%C-1.41%Ni steel
   (a) T.T.T. diagram
   (b) Partitioning coefficient at nucleation
   (c) Partitioning coefficient at growth

Fig. 13. Calculated results for Fe-0.81%C-1.41%Cr steel for \( \sigma_1 = 0.2, \sigma_2 = 0.0 \), [see Eq. (II.44)]
   (a) T.T.T. diagram
   (b) Partitioning coefficient at nucleation
   (c) Partitioning coefficient at growth

Fig. 14. Same as Fig. 13, but with \( \sigma_1 = 0.3, \sigma_2 = 0.0 \) (see Table 1).

Fig. 15. Same as Fig. 14, but with \( \sigma_1 = 0.4, \sigma_2 = 0.0 \) (see Table 1).
M: Alloying element  γ: Austenite
α: Ferrite  θ: Cementite

FIGURE 1
FIGURE 2

(a) 

(b) 

γ: Austenite
α: Ferrite
θ: Cementite

XBL 836-5924
FIGURE 3
FIGURE 4

(a) 

(b) 

(c) 

\[ \gamma: \text{Austenite} \]
\[ \alpha: \text{Ferrite} \]
\[ \theta: \text{Cementite} \]
$Z_i$: Concentration

$J^p_i$: Partitioning flux

$J^s_i, \phi$: Spike flux in front of $\phi$ phase

$\gamma$: Austenite
$\alpha$: Ferrite
$\Theta$: Cementite

**FIGURE 5**
FIGURE 6

\( \gamma \): Austenite
\( \alpha \): Ferrite
\( \theta \): Cementite
\[ \psi_i \]: Potential
\[ J^P_i \]: Partitioning flux
\[ \overline{J}^S_i \]: Average spike flux
\[ l_i \]: Length of path

\[ \gamma \]: Austenite
\[ \alpha \]: Ferrite
\[ \theta \]: Cementite

**FIGURE 7**
FIGURE 8
START

Read parameters

Preparation calculate Z:

T=1100

T=T-25

Maximize ΔF

Function ΔF

ΔF>0 ?

Yes

Maximize I'

Function I'

Maximize G'

Function G'

Xe calculation

Aging time calculation

No

T=650 ?

Yes

Plot

END

Figure 9-(a)
Figure 10.
Figure 11-(a).
Figure 11-(b).

Temperature (°K)

Partitioning coefficient

PEARLITE

BAINITE

XBL 8312-4868
Figure 11-(c).

Partitioning coefficient vs. Temperature (°K).

- PEARLITE
- BAINITE

XBL 8312-4869
Figure 12-(a).
Figure 12-(b).
Figure 12-(c).

NO PARTITIONING FOR BAINITE
Figure 13-(a).
Figure 13-(b).

Partitioning coefficient vs Temperature (°K)

PEARLITE

BAINITE
Figure 13-(c).
Figure 14-(a).
Figure 14-(b).
Figure 14-(c).
Temperature (°K)

Figure 15-(a).
Figure 15-(b).

Partitioning coefficient

Figure 15-(b).
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