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Edgewise growth kinetics of Widmanstätten precipitates

by

Edward P. Simonen

A Dissertation Submitted to the Graduate Faculty in Partial Fulfillment The Requirements for the Degree of DOCTOR OF PHILOSOPHY

Major: Metallurgy

Approved:

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CHAPTER I. INTRODUCTION

Origin of the Problem

Systems in nature are usually adaptable to minor changes in internal conditions and remain stable. However, if a change is large enough, the system will become overly stressed and is forced to reorganize itself to accommodate the excess internal stress. An ecosystem, for example, will be stable in spite of minor fluctuations in population. If the system is stressed in excess, however, by a complete extinction of one of its key members, the entire ecosystem will have to be reorganized to accommodate the new stress. Once the reorganization has taken place, the new system will then be the stable state.

Likewise, alloys also are usually stable to minor fluctuations in composition (population). However, large changes in composition typically necessitate a change in the alloy structure. The new crystalline arrangement will be such that the added stress (physical, chemical, etc., in nature) caused by the composition change will be relieved. The solid solution, consisting of the base metal and the alloying elements, is said to be supersaturated; and precipitation of a new solid solution occurs to relieve the supersaturation. A schematic phase diagram showing temperature and composition regions of stability for a single phase or a two-phase structure is illustrated in Figure 1.1. Change taking place in temperature or composition along the path of one of the indicated arrows results in the precipitation of a new phase.

Precipitation of one solid phase from another is favorable when such a reaction reduces the free energy of the system. In particular,
Figure 1.1. The schematic phase diagram illustrates method of precipitating one solid state phase from another by either increasing or decreasing the temperature or composition of a stable phase.
two characteristics of this transformation are of interest. First, when the free energy criteria is satisfied, the new phase can precipitate with the same composition as the original phase or of a different composition. A change in composition results in partitioning of elements and diffusion of these elements must accompany the transformation. Another characteristic of the new phase which is of importance is its shape. If strain is neglected and if the mobility and energy of the matrix-precipitate interface is independent of orientation, then the most efficient precipitate shape to accomplish the transformation is a sphere. For a spherical shape the most volume is transformed for the area of interface that has to be created. However, when strain in the lattice is important or when growth is not accomplished with equal facility in all directions, a nonspherical shape is observed. A barrier at the interface in only one orientation will result in a plate-shaped precipitate, whereas a barrier in all orientations except one will result in a needle-shaped precipitate. The two characteristics, partitioning of elements in solid solution and an observed growth barrier in one or more orientations resulting in plate-shaped or needle-shaped precipitates, thus defines the Widmanstätten structure for the purpose of the present dissertation. It is most easily identified by the observation of elongated precipitates which grow independently and are parallel to each other within a single grain.

History

The Widmanstätten structure was first observed and reported independently in the early 19th century by two European scientists, who
were interested in the nature of meteorites (1). William Tompson published observations of the structure in 1808, however von Widmanstätten's later publication in 1820 was more widely received. Hence, the structure unjustly acquired the name of the latter. The above observations were motivated primarily as a study of extraterrestrial phenomena and of the intrinsic beauty of the structure itself. The earliest observation of the Widmanstätten structure in a man-made alloy was made by Henry Clifton Sorby in 1863. This epoch discovery heralded the coming of metallurgy as a systematic science of relating physical properties of alloys to their microscopic appearance.

The development of crystallographic and x-ray techniques provided the means to determine the crystal orientation relationships between the precipitate and parent phases. Isothermal transformation experiments initiated by Bain indicated that these plate-like precipitates have a slow growth rate in contrast to the sheared rapid martensitic transformation. Interference microscopy has shown that the precipitates exhibit a surface tilt similar to that of martensite. In addition, transmission and scanning electron microscopy have provided valuable information concerning the structure and shape of Widmanstätten precipitates. A morphological description of the Widmanstätten structure has been discussed by Mehl and Dubé (2) and Aaronson (3).

Early experimental research on the Widmanstätten structure was restricted to observations of the particular orientation that the precipitates exhibited and to the identification of the matrix and precipitate phases. Osmund and Cartaud (4) presented the theory that
Widmanstätten plates should form on the matrix plane "of greatest rectilinear density." In the cases of meteoric iron and hypoeutectoid steels these planes are the octahedral planes, which are consistent with earlier theories describing the precipitate crystallography. The theory proved not to be general, for it was found in other systems that the crystalline nature of the precipitate is also of importance in determining the precipitate-matrix orientations. The 1920's and 1930's brought on an intense renewal of interest in the Widmanstätten transformation as it became recognized that precipitation from solid solution was responsible for age hardening. In addition, the development of X-ray diffraction made possible the study of crystal structures and crystal orientations. These studies, thus, were of value from both a scientific and technological viewpoint.

The diffusional characteristics of the problem were realized when Davenport and Bain (5) isothermally heat treated steel at temperatures where lower bainitic plates are observed. Their observations made a kinetic distinction between bainite (a Widmanstätten morphology) and martensite. The lengthening rate was theoretically predicted by Zener (6) and Hillert (7) by making a simple flux balance of solute at the tip interface to account for the necessary partitioning of elements and their subsequent diffusion. A variety of lengthening rate theories have been developed to describe the growth of a parabolically shaped precipitate (8-10). The theories differ in the rigor which is adhered to in considering the solute diffusion and the assumed interface concentrations, i.e., the partitioning criteria at the interface, which
determines the boundary condition for the diffusion equation. The most rigorous theory, which takes into account the proper concentration restrictions at the interface, is that of Trivedi (10). This treatment is used in the present analysis of lengthening kinetics in a variety of systems.

Transformation Mechanism

Thus, the advent of improved experimental techniques has produced the needed information to define the Widmanstätten structure with respect to its crystallographic orientation, morphology, and growth rate. In spite of these undisputed characteristics, the manner in which the constituents of the parent phase transfer into the second phase is of current controversy. The mechanism of the phase transformation has not been undisputedly determined, although many theories have been proposed to explain the plate shape of these precipitates. Earlier explanations such as the point effect of diffusion, elastic anisotropy, and interfacial energy anisotropy are not generally believed to be responsible. Two plausible theories remain to be debated. One is that the transformation takes place in a martensitic shear-like fashion, and the manifested plate shape is observed for the same reasons as is the case for martensitic plates. The other theory is that the interface at the sides is immobile, whereas it is proposed to be mobile in other orientations. Hence, anisotropy in the interfacial mobility is pronounced to be primarily responsible for the plate shape.

The first mechanism accomplished the transfer of atoms through a shear similar to the martensitic transformation. According to this
notion each solvent atom in the matrix has a predestined site in the precipitate, and it makes its transition in cooperation with its neighbors. The second mechanism transfers the atoms across a disordered boundary by a short range diffusional process, such that each atom makes the transition independently across a disordered portion of the interface by a thermally activated process. The interface at the platelet sides is believed to be semicoherent; thus atomistically the interface is stepped, the stepped region being disordered. Both theories rationalize the slow growth rate in terms of partitioning of a mobile species, which necessarily takes place to provide the driving force for the transformation. However, the theories differ in their interpretation of the apparent "shear", which could result from a real shear or from the coherent nature of the interface. Excellent reviews of these two mechanisms have been presented by Clark and Wayman (11) and Aaronson (12).

Both theories possess credibility. The shearists defend their mechanism on the basis of successful application of phenomenological martensitic theories, which predict the observed crystallography and surface relief. The ledgemen defend the short range diffusion mechanism by proposing that the interface is stepped on a fine scale, as has been observed in some systems. The observed surface relief results from the semicoherent terrace of the step, and the disordered ledge permits the necessary diffusion of atoms from one phase to the other. Growth is accomplished by the lateral motion of interfacial ledges, according to the ledge theory.
Purpose

The Widmanstätten morphology is observed in a great number of systems; and in fact, variations of the transformation are observed in single systems, including steel and brass. Of importance in the experimental study of the transformation are crystallographic orientation relationships, interfacial and precipitate structure, and the transformation kinetics. Although much effort has been made to understand individual transformations in certain systems, there is a need for a general approach which adequately describes the characteristics of all Widmanstätten transformations. A summary of pertinent experimental information in several systems is seen in Table 1. Of particular interest in the present thesis is to examine those alloys where kinetic data are available and to explore the possibility of discovering the germane phenomena which determines the kinetics and mechanism of growth of the Widmanstätten morphology. Such phenomena as diffusion, solid solution thermodynamics, interfacial structure, shape, mobility, transformation stresses, and diffusion are known to affect the kinetics. However, the role that each plays is not known. The present work seeks to determine the importance of each effect and to develop a feeling for extending the general theory to predict growth kinetics in systems where empirical data are not available. In addition, this information will provide an intelligence of how to control the evolution and growth of the Widmanstätten structure.

The control and study of the growth of the Widmanstätten structure has been and is of great importance to physical metallurgy. This is
Table 1. A summary is shown of some observed Widmanstätten structures. The kinetics are compared with volume diffusion and interfacial equilibrium. An interfacial energy of 200 ergs/cm² is assumed for all cases except Mo₂C, where 540 ergs/cm² applies.

<table>
<thead>
<tr>
<th>System</th>
<th>Transformation</th>
<th>Orientation</th>
<th>Kinetics</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe-C</td>
<td>γ(fcc) → α(bcc)</td>
<td>{111}_γ \parallel {110}_α, \langle 110 \rangle_γ \parallel \langle 111 \rangle_α</td>
<td>Slow</td>
<td>Kinetics are rationalized in this thesis</td>
</tr>
<tr>
<td>Meteoric Iron</td>
<td>γ(fcc) → α(bcc)</td>
<td>{111}_γ \parallel {110}_α, \langle 110 \rangle_γ \parallel \langle 111 \rangle_α</td>
<td>---</td>
<td>Composition is about Fe-8 wt % Ni</td>
</tr>
<tr>
<td>Fe-Mn-C</td>
<td>γ(fcc) → Upper bainite</td>
<td>{111}_γ \parallel {110}_α, \langle 211 \rangle_γ \parallel \langle 001 \rangle_α</td>
<td>Slow (13)</td>
<td>Orientation determined in Fe-Mn-C alloy (14)</td>
</tr>
<tr>
<td>Fe-Ni-C</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe-Ni-Mo-C</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe-C</td>
<td>γ(fcc) → Lower bainite</td>
<td>{111}_γ \parallel {110}_α, \langle 110 \rangle_γ \parallel \langle 111 \rangle_α</td>
<td>Slow (15)</td>
<td>Orientation determined in Fe-Mn-C alloy (14)</td>
</tr>
<tr>
<td>Fe-Mn-C</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe-Ni-C</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe-Ni-Mo-C</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe-Cr-C</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe-C</td>
<td>γ(fcc) → Fe₃C</td>
<td>{001}<em>Fe₃C is parallel to broad faces. \langle 112 \rangle is appr. parallel to \langle 100 \rangle</em>{Fe₃C}</td>
<td>Fast (16)</td>
<td>Habit plane is not unique</td>
</tr>
<tr>
<td>Fe-Mo-C</td>
<td>γ(fcc) → Mo₂C</td>
<td></td>
<td>Correct (17)</td>
<td>Needle shape observed</td>
</tr>
</tbody>
</table>
Table 1 (Continued)

<table>
<thead>
<tr>
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<th>Transformation</th>
<th>Orientation</th>
<th>Kinetics</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe-P</td>
<td>$\alpha$(bcc) → $\text{Fe}_3!^P$</td>
<td>Plates are parallel to ${12,1,4}_\alpha$</td>
<td>----</td>
<td>----</td>
</tr>
<tr>
<td>Fe-N</td>
<td>$\alpha$(bcc) → $\gamma$(fcc)</td>
<td>----</td>
<td>Fast (18)</td>
<td>Precipitates results from a gas-metal reaction</td>
</tr>
<tr>
<td>Fe-N (19)</td>
<td>$\alpha$(bcc) → $\text{Fe}_4!^N$</td>
<td>${210}<em>\alpha$ parallel to ${112}</em>{\text{Fe}_4!^N}$</td>
<td>----</td>
<td>----</td>
</tr>
<tr>
<td>Cu-Zn</td>
<td>$\beta$(bcc) → $\alpha$(fcc)</td>
<td>$\alpha$-needles parallel to $\langle111\rangle_\beta$</td>
<td>Fast (20)</td>
<td>Kinetics are rationalized in this thesis</td>
</tr>
<tr>
<td>Cu-Zn</td>
<td>$\beta$(bcc) → $\alpha'$(faulted fcc)</td>
<td>${110}<em>\alpha$ 4° from ${111}</em>\beta$</td>
<td>Fast (20)</td>
<td>Kinetics are rationalized in this thesis</td>
</tr>
<tr>
<td>Cu-Zn</td>
<td>$\alpha$(fcc) → $\beta$(bcc)</td>
<td>----</td>
<td>Fast</td>
<td>Appropriate diffusion data is not reliable</td>
</tr>
<tr>
<td>Cu-Zn</td>
<td>$\gamma$(cubic) → $\beta$(bcc)</td>
<td>----</td>
<td>----</td>
<td>Beta plates form within gamma precipitates (21)</td>
</tr>
<tr>
<td>Cu-Zn-Sn</td>
<td>$\beta$(bcc) → $\gamma$(cubic)</td>
<td>----</td>
<td>----</td>
<td>Plate tip shows instability (22)</td>
</tr>
<tr>
<td>Cu-16.5 at. % Sn</td>
<td>$\gamma$(bcc) → $\alpha'$(faulted hcp) + $\delta$(cubic)</td>
<td>----</td>
<td>----</td>
<td>Microstructure like upper bainite (23)</td>
</tr>
<tr>
<td>Cu-11.7 wt % Al</td>
<td>$\beta'$(bcc) → $\alpha'$(fcc) or at low temp. $\beta'$(bcc) → $\alpha'$(fcc) + $\gamma$(cubic)</td>
<td>----</td>
<td>----</td>
<td>Microstructure like upper bainite (24)</td>
</tr>
<tr>
<td>System</td>
<td>Transformation</td>
<td>Orientation</td>
<td>Kinetics</td>
<td>Comments</td>
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<td>-----------------</td>
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<td>----------</td>
<td>---------------------------------------------------------------------------</td>
</tr>
<tr>
<td>Cu-Si</td>
<td>$\alpha$(fcc) $\rightarrow$ $\gamma$(cubic)</td>
<td>Plates not parallel to $[111]_\alpha$</td>
<td>----</td>
<td>Observed orientation violates the theory of Osmund and Cartaud (25)</td>
</tr>
<tr>
<td>Cu-Ag</td>
<td>$\alpha_{Cu}$(fcc) $\rightarrow$ $\alpha_{Ag}$(fcc)</td>
<td>-----</td>
<td>-----</td>
<td>Precipitation of one terminal solid solution from the other exhibits the Widmanstätten structure (26)</td>
</tr>
<tr>
<td>Cu-Cr</td>
<td>$\alpha_{Cu}$(fcc) $\rightarrow$ $\alpha_{Cr}$(bcc)</td>
<td>-----</td>
<td>-----</td>
<td>Ledges are observed (27)</td>
</tr>
<tr>
<td>Cu-2 wt % Be</td>
<td>$\alpha$(fcc) $\rightarrow$ $\beta$(bcc)</td>
<td>One $\langle 100 \rangle_{bcc}$ axis is near $\langle 100 \rangle_{bcc}$, other two are near $\langle 110 \rangle_{bcc}$</td>
<td>-----</td>
<td>Phenomenological martensite theory predicts orientation (28)</td>
</tr>
<tr>
<td>Al-4 wt % Cu</td>
<td>$\alpha$(fcc) $\rightarrow$ $\sigma'$(bct)</td>
<td>${ 010 }<em>\alpha \parallel { 001 }</em>{\sigma'}$ \hspace{1cm} Fast (29)</td>
<td></td>
<td>Ledges are observed</td>
</tr>
<tr>
<td>Al-15 wt % Ag</td>
<td>$\alpha$(fcc) $\rightarrow$ $\gamma$(hcp)</td>
<td>${ 111 }<em>\alpha \parallel { 0001 }</em>\gamma$</td>
<td>-----</td>
<td>Ledges are observed (30)</td>
</tr>
<tr>
<td>Al-1.5 wt % MgSi</td>
<td>$\alpha$(fcc) $\rightarrow$ $\beta_{Mg,Si}$ (cubic)</td>
<td>${ 100 }<em>\alpha \parallel { 100 }</em>\beta$</td>
<td>-----</td>
<td>Ledges are observed (31)</td>
</tr>
<tr>
<td>Ti-Cr (32)</td>
<td>$\beta$(bcc) $\rightarrow$ $\text{TiCr}_2$</td>
<td>-----</td>
<td>-----</td>
<td>Alloy has eutectoid (33) transformation similar to steel</td>
</tr>
<tr>
<td>System</td>
<td>Transformation</td>
<td>Orientation</td>
<td>Kinetics</td>
<td>Comments</td>
</tr>
<tr>
<td>----------</td>
<td>---------------------------------</td>
<td>-------------</td>
<td>----------------</td>
<td>--------------------------------------------------------------------------</td>
</tr>
<tr>
<td>Ti-Cr</td>
<td>$\beta$(bcc) $\rightarrow$ $\alpha$(hcp)</td>
<td>...</td>
<td>Slow (34)</td>
<td></td>
</tr>
<tr>
<td>Ti-Mo (3)</td>
<td>$\beta$(bcc) $\rightarrow$ $\alpha$(hcp)</td>
<td>...</td>
<td>...</td>
<td></td>
</tr>
<tr>
<td>Co-46 at. %</td>
<td>$\alpha$(fcc) $\rightarrow$ (fct ordered)</td>
<td>...</td>
<td>Order-disorder transformation (35)</td>
<td></td>
</tr>
<tr>
<td>Pt</td>
<td>$\beta$(complex tetr.) $\rightarrow$ $\alpha$(orthorhombic)</td>
<td>...</td>
<td>...</td>
<td>Alloy also exhibits a slow isothermal low temperature martensitic transformation (36)</td>
</tr>
<tr>
<td>U-Cr</td>
<td>$\beta$(bcc) $\rightarrow$ $\alpha$(fcc)</td>
<td>...</td>
<td>...</td>
<td>See Reference 37</td>
</tr>
<tr>
<td>Ag-Cd</td>
<td>$\beta'$(bcc) $\rightarrow$ $\alpha$(fcc)</td>
<td>...</td>
<td>...</td>
<td>See Reference 38</td>
</tr>
<tr>
<td>Mg-Mg$_2$Sn</td>
<td>$\alpha$(hcp) $\rightarrow$ Mg$_2$Sn</td>
<td>...</td>
<td>...</td>
<td>See Reference 38</td>
</tr>
<tr>
<td>Pb-Sb</td>
<td>$\alpha_{Pb}$(fcc) $\rightarrow$ ${111}<em>{Pb}$$\parallel$${001}</em>{Sb}$</td>
<td>...</td>
<td>...</td>
<td>See Reference 38</td>
</tr>
</tbody>
</table>
due primarily to the effects that the structure has on mechanical properties. It may enhance the strength of an alloy, as is the case in Al-4% Cu; or it may reduce the ductility, as is the case in Widmanstätten ferrite in steels. Refractory metals may contain impurities such as hydrogen, nitrogen, and carbon, which may form metal impurity compounds as a Widmanstätten structure. These compounds can reduce the maximum ductility and possibly cause brittle fracture. This problem could be of great concern in the development of high temperature refractory alloys to be used in nuclear reactors. An understanding of the growth mechanism of the Widmanstätten structure will indicate what heat treatment, mechanical working, and alloying is necessary to prevent its evolution and growth.

The Widmanstätten structure has been, and still is, of importance in the development of steels. Mechanically, bainitic steels (a Widmanstätten structure) are almost comparable to tempered martensitic steels (39). The economic advantage that bainitic steels possess is that they can be formed on slow continuous cooling, as opposed to the rapid cooling and expensive aging that is necessary to produce a tempered martensitic structure. Lower bainitic structures will result when the appropriate alloying and thermal treatment is performed to retard the competitive transformations; namely, Widmanstätten ferrite, upper bainite, and pearlite. The lower bainitic structure is allowed to develop. The successful design of such alloying and thermal treatment practices are contingent upon a practical understanding of these transformation mechanisms and growth limiting processes. Since three
of the four possible transformations which may take place upon cooling of bainitic steels are of the Widmanstätten type, it is of value to develop a general theory to describe this type of transformation.

Thus, it can be seen from the previous discussion that the Widmanstätten transformation has been of interest to scientists for over one and a half centuries. Von Widmanstätten's observation of the intrinsic beautiful structure of meteoric iron, Sorby's metallurgical techniques and observations of steel, Davenport and Bain's isothermal transformation studies, and the investigations of others on age hardening and on decomposition of austenite have presented a wealth of information concerning the transformation. However, these same investigations have presented a dilemma concerning the growth mechanism. On the one hand, the observation of a surface relief and the precipitate-matrix orientation relationships suggest a shear mechanism similar to martensite. On the other hand, the surface relief and interfacial orientation relationships may be a consequence of the coherency of the interface such that growth takes place by the lateral motion of steps, whose terraces are semicoherent and ledges and kinks are incoherent.

It is the purpose of this thesis to examine the lengthening rates of Widmanstätten precipitates found in several systems and to analyze these rates to determine the role of diffusion, character of the interface, and solid solution thermodynamics. The thesis in part is intended to be an algorithm in that it will demonstrate procedures and considerations which must be taken into account in the study of diffusional growth of precipitates from supersaturated solutions.
The thesis is also intended to be heuristic, in that a general attack on the mechanism and growth of the Widmanstätten structure is undertaken to determine what further research is needed before a successful general theory of Widmanstätten precipitation can be propounded.
CHAPTER II. EXPERIMENTAL PROCEDURE AND RESULTS

Alloy Preparation

Iron-carbon alloys, whose compositions are given in Table 2 used in this investigation, were prepared at the Ford Motor Company by vacuum melting and casting. The specimens, 6 mm x 6 mm x 0.8 mm, were austenitized for 30 minutes at 1300°C in a graphite-deoxidized, argon-protected bath of molten BaCl₂.

The copper-zinc specimens were prepared from high purity copper and zinc in a quartz tube sealed under a rough vacuum of about $10^{-3}$ Torr. To protect the quartz tube, the assembly was sealed in an inconel tube in a helium atmosphere. The capsule was then placed in a rocker furnace and heated to a temperature above the alloy melting point for one day. The alloy was removed from the furnace and allowed to air cool. Sections from the bulk alloys were hot rolled 90% into sheets from which the specimens, approximately 3.0 mm x 6.5 mm x 0.2 mm, were cut. The 38.1 wt % Zn alloy was hot rolled at 475°C and homogenized at 475°C from one to two days. The 40.7 wt % Zn alloy was hot rolled at 500°C and homogenized at 800°C for several minutes, whereas the 43.7 wt % Zn alloy was hot rolled at 525°C and homogenized at 600°C for an hour. The given compositions were determined from chemical analyses. A comparison with the original compositions indicated that some zinc was lost during the preparation of all three alloys. The homogenization time was chosen to insure that diffusion would take place over a distance greater than the observed grain size. The diffusion distance
Table 2. The designation and composition of the iron-carbon alloys used for the kinetic and radii measurements are shown. The compositions are in units of wt. %

<table>
<thead>
<tr>
<th>Designation</th>
<th>%C</th>
<th>%Si</th>
<th>%Mn</th>
<th>%P</th>
<th>%S</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>0.24</td>
<td>0.003</td>
<td>0.002</td>
<td>0.001</td>
<td>0.005</td>
</tr>
<tr>
<td>II</td>
<td>0.33</td>
<td>0.002</td>
<td>0.002</td>
<td>0.001</td>
<td>0.005</td>
</tr>
<tr>
<td>III</td>
<td>0.43</td>
<td>0.004</td>
<td>0.002</td>
<td>0.001</td>
<td>0.004</td>
</tr>
</tbody>
</table>
was taken to be $\sqrt{Dt}$, where $D$ is the diffusivity and $t$ is time. It is not desirable to homogenize for times longer than necessary, since some volatile zinc is lost from the sample. Homogenization was conducted in a lead bath with the samples wrapped in brass foil and was interrupted by quenching into a 10% NaOH solution at 0°C.

The iron-carbon alloys were isothermally heat treated for the specified time and temperature in a deoxidized lead bath and quenched into iced 10% brine. The copper-zinc samples were wrapped in brass foil of the same composition as the specimen and isothermally heat treated for the specified time and temperature in a lead bath and quenched into a 10% NaOH solution at 0°C.

Lengthening Rate Measurement Procedures

The length of the longest precipitate of interest was measured for each isothermal heat treatment. The slope of a plot of the longest plate (or needle) versus the time of transformation gives the lengthening rate. This assumes that the longest plate in each case was the first to nucleate, thus all measurements at a given temperature and composition are made with respect to the same time reference. Each specimen was polished and etched to reveal the precipitate and matrix. Typical photomicrographs of the precipitates of interest are shown in Figures 2.1-2.4. The procedure of polishing and etching was repeated several times on each specimen to insure that the longest plate was found and measured. This is necessary to overcome the statistical problem of making a good section of the sample such that the longest
Figure 2.1. Widmanstätten ferrite plates in an Fe-0.33% C alloy transformed at 650°C for 7 seconds. Magnification 400X
Figure 2.2. Widmanstätten alpha plates in a Cu-40.0 at. % Zn alloy transformed at 350°C for 30 seconds. Magnification 800X
Figure 2.3. Widmanstätten alpha needles in a Cu-43.0 at. % Zn alloy transformed at 300°C for 155 minutes. Magnification 800X
Figure 2.4. Widmanstätten beta plates in a Cu-37.4 at. % Zn alloy transformed at 665°C for 120 seconds. Magnification 1000X
dimension of the longest plate is revealed. The samples were mechanically polished with 600 grit paper, Linde A powder, and Linde B powder. The etching of the iron-carbon was done with nital, whereas a solution of 5 g FeCl₃, 96 ml ethyl alcohol, and 2 ml HCl was used to etch the brass specimens.

In the cases of iron-carbon and the α→β transformation in brass, a different specimen was reacted for each specified time. However, in the case of the β→α transformation a single specimen was treated for each lengthening rate measurement. In this manner, the transformation was interrupted by quenching for metallographic observation and then reheated to the reaction temperature to further transform the specimen.

Hot Stage Procedure

Preliminary hot stage metallographic motion pictures were taken of the β→α (needle) transformation in a sample whose composition was about 42 at % Zn. The in situ observation of the β→α transformation in brass is possible because it produces a surface relief effect on a polished surface. A highly polished surface was obtained by electropolishing in a 60 ml H₂O, 40 ml phosphoric acid solution.

The design and description of the hot stage experiment constructed as a part of this research will now be discussed. The Leitz vacuum heating stage 1750 is used with a Leitz metallux microscope. The microscope has an eyepiece attachment with a two-way prism, which allows the sample to be viewed simultaneously as it is being photographed.
with an Eastman Cine-Kodak Special II movie camera. The film used in this investigation was Kodak Double X Negative Type 7222, which provided excellent pictures with normal lighting and contrast settings on the microscope. A hot stage vacuum of about $10^{-5}$ Torr was obtained with a Welch Duo Seal roughing pump and a Veeco oil diffusion pump. The experiment is also capable of providing a high purity helium quench, which was not used in the present work.

The sample is heated by its own resistance to the desired temperature which is measured on a millivolt recorder with a Pt-13% Rh thermocouple spot welded to the bottom of the sample. The $\alpha - \gamma$ transformation in pure iron was observed, and the temperature was measured to verify that the temperature measurements were correct. The stage is provided with water cooling for high temperature observations.

Results

The experimental results of the length versus time measurements are shown in Figures 2.5-2.7. The slopes of these plots yield the edgewise growth velocity and are shown in Table 3 along with Hillert's data. The data taken at $700^\circ$C which were not from Hillert were obtained from Simonen, Aaronson, and Trivedi (41). The slopes were calculated using a linear least squares analysis of the length versus time data.

The length versus time data for precipitate growth in brass are shown in Figures 2.8-2.11. The edgewise growth kinetics of alpha precipitating from beta brass are shown in Figures 2.8-2.10, whereas
Figure 2.5. Length of longest ferrite plate versus time for the indicated alloys at 650°C
Figure 2.6. Length of longest ferrite plate versus time for the indicated alloys at 550°C
Figure 2.7. Length of longest ferrite plate versus time for the indicated alloys at 450°C
Table 3. The measured Widmanstätten ferritic edgewise growth rate results are shown with those of Hillert (40).

<table>
<thead>
<tr>
<th>T°C</th>
<th>0.24% C</th>
<th>0.29% C</th>
<th>0.33% C</th>
<th>0.43% C</th>
<th>0.49% C</th>
</tr>
</thead>
<tbody>
<tr>
<td>700</td>
<td>2.1</td>
<td>1.6&lt;sup&gt;a&lt;/sup&gt;</td>
<td>1.3</td>
<td>0.6</td>
<td>0.2&lt;sup&gt;x&lt;/sup&gt;</td>
</tr>
<tr>
<td>650</td>
<td>2.2</td>
<td>2.2&lt;sup&gt;a&lt;/sup&gt;</td>
<td>1.5</td>
<td>0.8</td>
<td>1.0&lt;sup&gt;x&lt;/sup&gt;</td>
</tr>
<tr>
<td>550</td>
<td>2.5</td>
<td></td>
<td>2.2</td>
<td>1.3</td>
<td></td>
</tr>
<tr>
<td>450</td>
<td>3.2</td>
<td></td>
<td>2.3</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<sup>a</sup>Hillert (40).
Figure 2.8. Alpha plate length versus reaction time in a 40.0 at. % Zn alloy
Figure 2.9 Precipitate length versus reaction time for plate growth in a 40.0 at. % Zn alloy and needle growth in a 43.0 at. % Zn alloy.
Figure 2.10. Length of longest beta side plate versus reaction time at 665°C for a 37.4 at. % Zn alloy.
Figure 2.11. Half length of an alpha needle versus transformation time. This data was taken with a hot stage metallograph.
Figure 2.11 describes the lengthening of beta sideplates growing from the alpha phase. The lengthening of an alpha needle was observed in the hot stage and the results are plotted in Figure 2.10. The velocity is seen to be independent of time and thus supports the assumption that the lengthening process is a steady state process. The velocity results from the present and other investigations on the beta to alpha transformation are given in Table 4 and 5.
Table 4. The edgewise growth rates of alpha needles precipitating from beta brass are shown as reported by Repas and Hehemann (20). The present results and those of Purdy (42) are also shown.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Alloy Composition at % Zn</th>
<th>Velocity cm/sec</th>
</tr>
</thead>
<tbody>
<tr>
<td>250</td>
<td>42.5</td>
<td>$1.3 \times 10^{-7}$</td>
</tr>
<tr>
<td>300</td>
<td>44.4</td>
<td>$5.0 \times 10^{-8}$</td>
</tr>
<tr>
<td>300</td>
<td>43.5</td>
<td>$3.3 \times 10^{-7}$</td>
</tr>
<tr>
<td>300</td>
<td>42.5</td>
<td>$1.7 \times 10^{-6}$</td>
</tr>
<tr>
<td>350</td>
<td>44.4</td>
<td>$1.2 \times 10^{-6}$</td>
</tr>
<tr>
<td>350</td>
<td>43.5</td>
<td>$3.3 \times 10^{-6}$</td>
</tr>
<tr>
<td>350</td>
<td>42.5</td>
<td>$1.5 \times 10^{-5}$</td>
</tr>
<tr>
<td>350</td>
<td>42.0&lt;sup&gt;a&lt;/sup&gt;</td>
<td>$2.3 \times 10^{-5}$</td>
</tr>
<tr>
<td>350</td>
<td>41.1</td>
<td>$6.7 \times 10^{-5}$</td>
</tr>
<tr>
<td>400</td>
<td>44.4</td>
<td>$5.0 \times 10^{-6}$</td>
</tr>
<tr>
<td>400</td>
<td>44.1&lt;sup&gt;b&lt;/sup&gt;</td>
<td>$1.6 \times 10^{-5}$</td>
</tr>
<tr>
<td>400</td>
<td>43.5</td>
<td>$1.7 \times 10^{-5}$</td>
</tr>
<tr>
<td>400</td>
<td>42.5</td>
<td>$1.0 \times 10^{-4}$</td>
</tr>
<tr>
<td>400</td>
<td>41.1&lt;sup&gt;b&lt;/sup&gt;</td>
<td>$4.7 \times 10^{-4}$</td>
</tr>
<tr>
<td>400</td>
<td>41.1</td>
<td>$3.3 \times 10^{-4}$</td>
</tr>
<tr>
<td>450</td>
<td>43.5</td>
<td>$8.3 \times 10^{-5}$</td>
</tr>
<tr>
<td>450</td>
<td>42.5</td>
<td>$5.0 \times 10^{-4}$</td>
</tr>
<tr>
<td>500</td>
<td>43.5</td>
<td>$3.3 \times 10^{-5}$</td>
</tr>
<tr>
<td>500</td>
<td>42.5</td>
<td>$6.7 \times 10^{-4}$</td>
</tr>
</tbody>
</table>

<sup>a</sup>Present.<br><sup>b</sup>Purdy (42).
The edgewise growth rates of alpha plates precipitating from beta brass are shown as reported by Repas and Hehemann (20). The present results and those of Hornbogen and Warlimont (43) are also included.

<table>
<thead>
<tr>
<th>Temperature °C</th>
<th>Alloy Composition at % Zn</th>
<th>Velocity cm/sec</th>
</tr>
</thead>
<tbody>
<tr>
<td>250</td>
<td>41.1</td>
<td>5.0 x 10^-7</td>
</tr>
<tr>
<td>250</td>
<td>41.0&lt;sup&gt;a&lt;/sup&gt;</td>
<td>1.5 x 10^-6</td>
</tr>
<tr>
<td>250</td>
<td>40.0&lt;sup&gt;b&lt;/sup&gt;</td>
<td>4.0 x 10^-6</td>
</tr>
<tr>
<td>300</td>
<td>41.1</td>
<td>6.7 x 10^-6</td>
</tr>
<tr>
<td>300</td>
<td>40.0&lt;sup&gt;b&lt;/sup&gt;</td>
<td>1.8 x 10^-5</td>
</tr>
<tr>
<td>300</td>
<td>39.3</td>
<td>1.3 x 10^-4</td>
</tr>
<tr>
<td>350</td>
<td>40.0&lt;sup&gt;b&lt;/sup&gt;</td>
<td>9.0 x 10^-5</td>
</tr>
<tr>
<td>350</td>
<td>39.3</td>
<td>1.0 x 10^-3</td>
</tr>
</tbody>
</table>

<sup>a</sup>Hornbogen and Warlimont (43).

<sup>b</sup>Present.
CHAPTER III. THEORETICAL MODEL

Introduction

The Widmanstätten transformation is observed in several systems and is believed to possess certain common characteristics. These characteristics must be included in any valid general model which predicts the precipitate radius at the tip and the lengthening rate. Zener (6) was the first to analyze the lengthening rate of plates growing under the influence of the necessary diffusion of solute. His treatment was no more than an attempt to make a flux balance on the solute at the tip of the plate, taking into account the change in interfacial concentration due to its curvature. Hillert (7) used a similar treatment with the inclusion of a more mathematical rigorous description of the matrix solute concentration field for a cylindrically shaped interfacial tip. In the treatment the diffusion equation was satisfied in the matrix and the predicted velocity was made to be consistent with it. In addition, Hillert introduced more thermodynamic rigor in the description of the capillary boundary condition. Unfortunately, Hillert was forced to make several mathematical approximations in the treatment in order to solve the problem. Ivantsov (8) has solved the diffusion problem rigorously for an unrealistic isoconcentrate boundary, hence capillarity was not taken into proper account.

The Model of Trivedi

Recently Trivedi (10) has corrected Ivantsov's solution to take into account the effect of capillarity and interface kinetics. The
theory of Trivedi has the best mathematical rigor and is most consistent with the known and expected characteristics of the transformation; e.g., volume diffusion, thermodynamics, and a parabolic interfacial shape. Although the sides of the Widmanstätten plate or needle are parallel far from the tip, in the region of the tip the interface is observed to have the morphology of a parabola. In both Fe-C and Cu-Zn it has been observed that solute partitioning does accompany the transformation. It is assumed in the theory that the partitioning is consistent with equilibrium thermodynamics at the interface. Hence, the rate of flow of solute diffusion away from the interface must be equal to the rate of partitioning of solute at the interface. The theory satisfies this flux balance at the tip only, hence the theory will be less accurate when the effective diffusion distances are much larger than the physical dimension of the tip. To calculate the diffusional flux one must solve the diffusion equation in the matrix region given the concentration at the interface from equilibrium thermodynamics and interfacial kinetic considerations.

The appropriate differential equation which describes the concentration field in the matrix, as it is influenced by diffusion, is given in parabolic coordinates as

\[
\frac{\partial^2 c}{\partial s^2} + \frac{\partial^2 c}{\partial \eta^2} + 2\rho [g \frac{\partial c}{\partial s} - \eta \frac{\partial c}{\partial \eta}] = 0
\] (3.1)

where \(s\) and \(\eta\) are parabolic coordinates normal to the interface and
along the interface, respectively. The solute concentration is given
by \( c \) and the normalized velocity, \( p \), is called the peclet number. The
peclet number is equal to \( \frac{vp}{2D} \), where \( v \) is the edgewise growth velo-
city, \( p \) the tip radius and \( D \) the solute diffusivity. The concentration
at the interface, \( c_i \), is assumed to be dictated by equilibrium thermo-
dynamics and interface kinetics, hence it is proper to solve the above
equation for the following boundary condition at the precipitate
interface, i.e.,

\[
c_i = c_o - \left( \frac{c_o \Gamma}{p} \right) \left[ 1 + \eta_1^2 \right]^{-3/2} = \left( \frac{v}{\mu_o} \right) \left( 1 + \eta_1^2 \right)^{-1/2}; \tag{3.2}
\]

where the first term on the right, \( c_o \), is the equilibrium matrix con-
centration if normal motion of the interface required no interfacial
creation, as for a flat interface. The second term involving the
capillary constant, \( \Gamma \), corrects the interfacial concentration to take
into account interfacial creation for an interface growing normal to
itself having a radius curvature of \( p \). The third term involves the
kinetic parameter, \( \mu_o \), and takes into account the supersaturation that
is needed to advance the interface at a velocity, \( v \). The present prob-
lem is known as a Dirichlet problem, because the diffusion equation is
solved for an assumed interfacial boundary concentration. The solution
is given by Trivedi as

\[
\Omega_o = \sqrt{\pi p} e^{\text{Perfc}(\sqrt{p})} \left[ 1 + \frac{v}{v_c} \right] \Omega_1(p) + \left( \frac{\rho_c}{\rho} \right) \Omega_2(p), \tag{3.3}
\]
where $\Omega_0$ is the normalized supersaturation and is equal to 

$$\frac{(c_0 - c_\infty)}{(c_o - c_p)}.$$ 

$c_\infty$ and $c_p$ are the mole fraction of solute in the original homogeneous alloy and the equilibrium mole fraction of solute in the precipitate at a flat interface, respectively. $r^*$ is the equilibrium critical radius equal to $c_0 r/c_{\text{cg}} - c_{\infty}^*$ and represents the radius which produces a matrix interfacial concentration equal to $c_{\infty}$. $v_c$ is the critical velocity, which is the velocity the interface would move at if it were entirely interface controlled, thus

$$v_c = \mu_0 (c_0 - c_\infty).$$ (3.4)

$s_1(p)$ and $s_2(p)$ are complicated functions of $p$ and are given by Trivedi. Yost (44) has presented the following approximations for the functions

$$s_1(p) = 1/\pi p \quad \text{(3.5)}$$

$$s_2(p) = 2/\pi p \quad \text{(3.6)}$$

for the plate.

Although Equation 3.3 is consistent with the necessary volume diffusion caused by the solute partitioning, it does not uniquely predict a velocity and a radius for a given supersaturation. The theory predicts an infinite set of pairs of velocities and radii. A typical plot of velocity versus radius is shown in Figure 3.1 for a given
Figure 3.1. Calculated velocity versus radius is shown for the 0.24% C alloy at 700°C. Q is a measure of the importance of interfacial kinetics and is given by

$$\eta_{0}(c_{0}-c_{\infty})\rho_{C}/2D. \quad \sigma$$ is the assumed interfacial energy.
supersaturation. It is seen that a maximum in the plot exists, thus a plate having a radius of $\rho_{\text{max}}$ will grow at a maximum velocity. Zener has proposed that this is the velocity that nature seeks out to attain, hence it is assumed that the radius is chosen by nature so as to optimize the lengthening velocity. Equation 3.3 can be differentiated with respect to $\rho$, and terms involving $\partial v / \partial \rho$ are set equal to zero to obtain a second equation which is valid for the condition of maximum lengthening rate for a given $\Omega_0$. The two equations now determine uniquely a velocity and radius for a given $\Omega_0$. Equation 3.3, differentiated, produces the second equation which is

$$\frac{\partial \Omega_0}{\partial \rho} = 0 = \frac{\Omega_0}{2\rho} (2\rho + 1.0) - \Omega_0 \sqrt{\pi \rho} e^{-\rho} \text{erfc}(\sqrt{\rho})$$

$$+ \sqrt{\pi \rho} e^{-\rho} \text{erfc}(\sqrt{\rho}) \left[ \frac{\rho}{\sqrt{\rho}} S_1^{\prime}(\rho) + \frac{\rho}{\sqrt{\rho}} S_2^{\prime}(\rho) - \frac{\rho}{\sqrt{\rho}} S_2^{\prime}(\rho) \right], \quad (3.7)$$

where $S_1^{\prime}(\rho)$ and $S_2^{\prime}(\rho)$ are differentiated with respect to $\rho$ and have been calculated by Trivedi. Hence, the theory predicts the lengthening kinetics provided the following parameters are known: $c_0$, $c_\infty$, $c_\rho$, $D$, $\Gamma$, and $\mu_0$. All these terms are known from other independent experiments except the capillary constant, involving the interfacial energy and the kinetic parameter $\mu_0$. Comparison of the theory with empirical data allows for a determination of the interfacial energy and kinetic parameter. The equilibrium concentrations, $c_0$ and $c_\rho$, can be obtained from the phase diagram; and the capillary constant can be calculated.
from the assumed interfacial energy and the thermodynamics of the precipitate and matrix phases. The diffusivity is measured independently; and if found to be a function of concentration, a diffusivity must be used which is averaged over the concentration range of interest.

Trivedi has also solved the same problem for the needle morphology, a paraboloid of revolution. In this case the supersaturation is dependent on the Peclet number as

\[ \Omega_c = p e^P E_1(p)[1 + (v/v_c)\Omega_1(p) + (\rho'_{c}/\rho)\Omega_2(p)] \]  

(3.8)

where \( E_1 \) is the exponential integral function and \( \rho'_{c} \) is the critical radius for the needle. \( R_1(p) \) and \( R_2(p) \) are complicated functions of \( p \) and are given by Trivedi. The equation which corresponds to Equation 3.7 for the plate is, for the needle,

\[ \frac{d\Omega_c}{dp} = 0 = \frac{\Omega_c}{2p} (2p + 2) - \Omega_c pe^P E_1(p) \]

\[ + pe^P E_1(p)[\frac{v}{v_c} R_1^1(p) + \frac{\rho}{\rho} R_2^2(p) - \frac{\rho_c}{\rho} S_2(p)] \]

(3.9)

where \( R_1^1(p) \) and \( R_2^2(p) \) are differentiated with respect to \( p \) and have been calculated by Trivedi. Together Equations 3.8 and 3.9 can be solved to predict a unique velocity and radius for a given supersaturation for the edgewise growth of a needle-shaped precipitate.
The unexpected behavior of the \( v \) versus \( p \) plot shown in Figure 3.1 deserves comment. It is usually believed that the velocity should go to zero for the critical radius, \( p_c \). However, in this case it is observed that a minimum radius exists, below which growth is not possible. This minimum radius is larger than the critical radius. If the interface were isoconcentrated, the minimum in the radius would not appear. It is only because of the competition between the nonisoconcentrate boundary and the point effect of diffusion that the minimum occurs.

The capillary modified nonisoconcentrate boundary physically causes solute to be transported from the rear of the plate to the tip. The point effect of diffusion physically transports solute away from the tip. In the region of radii between the critical radius and the minimum radius the situation exists where solute is being transported toward the tip as a result of capillarity faster than the point effect of diffusion can transport it away from the tip. Hence, a pile up of solute is created in advance of the tip interface. This is the physical reason for the nonexistence of growth velocities for plates having a radius less than the predicted minimum.

The normalized supersaturation for the plate and needle is seen to be divided into three terms in Equations 3.3 and 3.8. The first term is the isoconcentrate solution and represents the supersaturation dissipated in volume diffusion. The second and third terms account for the driving force lost in interfacial migration and interfacial creation. Thus, the experimental determination of the edgewise growth
velocity and tip radius permits the theoretical evaluation of the dissipative processes which are governing the growth.
CHAPTER IV: WIDMANSTÄTTERN GROWTH OF FERRITE IN Fe-C ALLOYS

Introduction

The diffusional decomposition of austenite is known to occur by several different mechanisms resulting in a variety of possible microstructures. The mechanical properties of steels are intimately related to microstructure, hence great technological benefit can be realized from an understanding of the nature of the decomposition of austenite. It is not surprising that studies of these transformations have been of major interest to physical metallurgists for many decades.

Figure 4.1 shows the composition and temperature regions where transformation products form from austenite by diffusional processes. Whether or not a single phase, ferrite or cementite, or a two phase structure, pearlite or bainite, is observed is dependent on alloy composition and isothermal heat treating temperature. Of particular interest in this work is the region where Widmanstätten ferrite is the predominant precipitate phase.

The crystallography of the Widmanstätten plate is well established and has been found to be in agreement with the Kurdumov-Sachs orientation, \([111]_\gamma \parallel [110]_\alpha^\prime, \langle 110 \rangle_\gamma \parallel \langle 111 \rangle_\alpha^\prime\). Ko and Cottrell (45) have concluded that the surface relief exhibited by the transformation indicates that it proceeds by a shear mechanism. The partitioning of carbon between austenite and ferrite has been established by Hillert (40). He made use of the fact that the \(M_s\) temperature is dependent on composition, hence the observed absence of martensite close to pre-existing Widmanstätten ferrite indicated that there is a carbon
Figure 4.1. Possible modes of diffusional decomposition of austenite
rich region surrounding the Widmanstätten plate. The enriched region results from partitioning associated with the transformation. Thus, any model which describes the Widmanstätten ferritic transformation must be consistent with the observed crystallography, surface relief, and carbon partitioning at the interface.

Kaufman, Radcliffe, and Cohen (46) (KRC) were the first to examine the lengthening kinetics of ferritic plates using the Zener-Hillert model and a thermodynamic model of their own to describe the solid solution, austenite. They compared their predictions with experimental data for the lengthening rate of lower and upper bainite and Widmanstätten ferrite. The conclusion was drawn that all three transformations could be described by a continuous model through the entire temperature range. The model stated that the lengthening rate was determined by volume diffusion away from the leading edge of the plate; and that the carbide precipitation, in the case of bainite, does not influence the edgewise growth. The tip was predicted to have an interfacial energy of 200 ergs/cm$^2$, corresponding to a semicoherent interface.

Paxton and Pound (47) have compared the measured lengthening rates with predictions made by the Zener theory and thermodynamic approximations made by themselves. They concluded volume diffusion properly describes the kinetics if an interfacial energy of 800 ergs/cm$^2$ is assumed; this represents a disordered interface. Townsend and Kirkaldy (48) have compared the edgewise growth rates and spacing of Widmanstätten plates with diffusional models and have concluded that
volume diffusion and capillarity properly describe the evolution and growth of Widmanstätten ferrite if an interfacial energy of 755 ergs/cm² is assumed. The lengthening rates were predicted from the Zener-Hillert model utilizing the capillarity predictions of Hillert (7). Thus, depending on the approximations used in predicting the effect of capillarity and volume diffusion, it is possible to rationalize the measured kinetics on the basis of interfacial equilibrium and volume diffusion of carbon. The various analyses predict either a semicoherent or a disordered interface and are in disagreement with each other. Hence, the need has arisen to examine the lengthening kinetics taking into account the thermodynamics of austenite and volume diffusion of carbon rigorously. The following discussion seeks to satisfy that need.

**Interfacial Creation and Thermodynamics**

A proper thermodynamic description of austenitic and ferritic solid solutions at hypoeutectoid temperatures is crucial in the successful application of models predicting the kinetics of diffusional transformations. The description is necessary to presage the metastable phase diagram and to predict the effect of curvature on the interfacial equilibrium criteria.

Since austenite is not a stable phase at temperature below the eutectoid temperature, it is not possible to obtain the necessary thermodynamic experimental data in this temperature region. The data must be obtained at hypereutectoid temperatures and extrapolated to
lower temperatures. The extrapolation process can only be performed if a model is available to relate iron and carbon chemical potentials to temperature and composition. Such a model is made to fit hypereutectoid data, then the same fit is used to presage hypoeutectoid behavior. The various models differ in methods of introducing non-ideality into the statistical thermodynamic description of the austenitic and ferritic solid solutions.

A recent review of the thermodynamic properties of iron-carbon austenite has been presented by Ban-ya, Elliot, and Chipman (49) (BEC). These authors have experimentally determined the activity of carbon in austenite at 1150°C for concentrations up to 2.1% C. A total of twelve different statistical models were tested against this data, and three were found to represent the data satisfactorily over a wide range of concentration. The proper model of Aaronson, Domian, and Pound (50) (ADP) was utilized in the present analysis. One less appropriate model, that of Kaufman, Radcliffe, and Cohen (KRC), is also included in the present analysis due to its previous use in other similar transformation analyses. The results of an assumed thermodynamic model enter the kinetic calculation in the following two ways: first, in the prediction of the effect of curvature on interfacial equilibrium; and second, in the prediction of the metastable phase diagram. The ADP and KRC models are consistent with respect to the predictions of the curvature effect but differ with respect to the phase diagram extrapolation with decreasing temperature. Both models predict identical results in the dilute solution limit, but differ in both formulation
and predictions at higher concentrations.

The KRC model assumes that an interstitial carbon atom can exclude a certain number of neighboring sites from occupancy. The number of such sites is included as an adjustable parameter which is determined from hypereutectoid thermodynamic data. The model, thus, assumes that the number of sites excluded at hypereutectoid temperatures is the same as those excluded at hypoeutectoid temperatures. In contrast, the ADP model utilizes the Lacher-Fowler-Guggenheim equation, which assumes that each interstitial carbon atom can interact with other carbon atoms with a repulsive or attractive energy. The energy of repulsion or attraction is allowed to be an adjustable parameter and is determined from a hypereutectoid fit of the thermodynamic data. The interaction energy is assumed to be proportional to absolute temperature, and the data is extrapolated to hypoeutectoid temperatures. The conclusion of BEC, that the ADP model is more satisfactory, does not necessarily mean that the assumptions of the model are more physically realistic. It does reflect that the model is more flexible and can be made to fit the data over a wider concentration range. Hence, the predictions of ADP are expected to be particularly more reliable for higher concentrations. Thus, it is important in the present work to compare the prediction of both ADP and KRC and to give greater weight to those of ADP.

Before exploring the effects of thermodynamics and volume diffusion on the lengthening kinetics of Widmanstätten ferritic precipitates, it will be necessary to review and develop the necessary formulations which will account for the energy consumed in creating
austenite-ferrite interface during the growth of a curved ferritic precipitate.

Herring (51) has shown that an atom at a curved interface has an excess free energy over that at a flat interface of the amount

\[ \Delta G = \sigma K . \]  

(4.1)

\( \Delta G \) is the excess free energy; \( \sigma \) is the surface energy; and \( K \) is the curvature of the interface. Consequently, equilibrium across a curved interface separating two condensed phases is insured by equating the total chemical potential, dependent on both composition and curvature, across the interface. This curvature dependent correction alters the equilibrium concentrations at the curved interface separating the two phases of an alloy. Zener (6) was first to point out the importance of this effect on the growth kinetics of precipitates growing by volume diffusion. The purpose of the present discussion is to determine a proper analytic expression for the equilibrium concentrations of carbon and iron in austenite and ferrite along a curved interface. These results can then be applied to the growth of ferritic precipitates.

Several treatments have been given for the iron-carbon system (7,46,47,52,53). Solution of the problem depends on knowledge or assumptions concerning the dependence of chemical potential on concentration in the two phases, i.e., deviation from ideality in the metastable region of interest. Additional assumptions are made by some authors as to the atomic volumes and atomic mobilities. Most
predictions render their results in a manageable form of the type

$$\gamma_p = C_o^{\gamma} (1 - \gamma k) ,$$  \hspace{1cm} (4.2)

where $C_p^{\gamma}$ is the equilibrium concentration in the austenite at a curved interface having a radius of curvature $\rho$. $C_o^{\gamma}$ is the equilibrium concentration in the austenite at a flat interface.

The most naive approach is to assume that austenite is an ideal dilute solution with equilibrium established across the interface with respect to the mobile species, carbon, only. Iron is assumed to be too immobile to adjust to equilibrium. Such an approach renders the familiar Gibbs-Thompson equation with the capillarity constant given by

$$\Gamma = \frac{\sigma V C^\alpha}{RT} .$$  \hspace{1cm} (4.3)

$V_c^\alpha$ is the atomic volume of carbon in the ferrite phase, $R$ is the gas constant, and $T$ is the absolute temperature. Hillert (7) was the first to improve this approach by describing the thermodynamic behavior of carbon in austenite according to Smith's (54) hypereutectoid austenitic data. In the analysis equilibrium was assumed to be established with respect to carbon, and the concentration of the precipitate was fixed at a constant value. Hillert predicted the capillarity constant to be as follows where $k$ is a constant:

$$\Gamma = \frac{\sigma V C^\alpha}{\gamma_{Fe} C_o^{\gamma} RTk} .$$  \hspace{1cm} (4.4)
Friedel and Mullins (52) approached the problem by assuming that the atomic volume of carbon was negligible and that the theory of ideal dilute solutions could be applied. Equilibrium was established with respect to both iron and carbon. They allowed the composition of the precipitate to vary, hence the analysis also predicts the concentration inside the precipitate at a curved interface. They concluded that the capillarity constant is

$$\Gamma = \frac{-\alpha}{\sigma V_{Fe}} \left( \frac{c_{\gamma} - c_{\alpha}}{\rho} \right) RT$$

(4.5)

The method of Paxton and Pound (47) resembles that of Hillert; in addition, they allowed the chemical potential of iron to vary with curvature. Their treatment, consequently, introduces the change in free energy for the austenite to ferrite transformation in pure iron, $\Delta G_{Fe}^{\gamma \rightarrow \alpha}$. This approximate analysis gives the capillarity constant as

$$\Gamma = \frac{-\alpha}{\sigma V_{Fe}} \left( \frac{c_{\gamma} - c_{\alpha}}{\rho} \right) \left( \frac{\Delta G_{Fe}^{\gamma \rightarrow \alpha}}{\sigma V_{Fe}} \right)$$

(4.6)

It is necessary in the Paxton and Pound analysis to let the concentration in the precipitate approach zero, therefore the precipitate concentration cannot be predicted from this theory. The hypereutectoid chemical potential data of Darken and Smith (55) was used to describe the thermodynamics of the austenite.
All the above treatments encounter the difficulty of establishing a means of extrapolating the thermodynamic data from the hypereutectoid temperatures to the metastable hypoeutectoid temperatures. KRC have developed an extrapolation which utilizes the knowledge of statistical thermodynamics of interstitial solid solutions. The extrapolation is an extension of the phase diagram which has been modified to agree with a theory of interstitial solid solutions. Thus the KRC prediction has been thought to be more consistent with the real behavior of these phases.

Trivedi and Pound (53) have utilized the theory of KRC and have derived two transcendental expressions relating the interfacial concentrations to curvature. Although their results have to be considered most rigorous, they are not in a manageable analytical form which can be utilized in transformation theories. It is, therefore, of importance to compare the analytical results of the previous theories with that of Trivedi and Pound to determine which agrees best. Such an analysis reveals that Paxton and Pound's results agree well at high temperatures, near the eutectoid temperature. This is expected as Paxton and Pound's austenite solution extrapolation is not as rigorous as that of KRC. To obtain the rigor of Trivedi and Pound, the results of Paxton and Pound were corrected by introducing the adjustable parameter $B$. The factor $B$, $B = -1.19778 \times 10^{-5} (T - 852)^2 + 1.699733 \, \, \, (4.7)$, was chosen to maintain the manageable analytic form of Equation 4.1.
while not losing any of the rigor introduced by KRC. The capillarity constant is now given by

$$\Gamma = \frac{\alpha \nu}{RT} \left( -\frac{RT}{\Delta G_{\text{Fe}}} - B \right).$$ (4.8)

As was discussed previously, BEC have recently shown that the thermodynamic treatment of ADP is consistent with experimental data over a wider composition range than the KRC treatment. The treatments of ADP and KRC were compared and found to predict capillarity constants which were in agreement within an error of 10%. Thus, it was concluded that the factor B was consistent with both the ADP and KRC treatments with the worst error being about 3% for KRC and 10% for ADP.

The capillarity constants normalized with respect to that of Friedel and Mullins (52) are plotted in Figure 4.2 to indicate how the various treatments disagree with the more rigorous Trivedi and Pound results as a function of temperature. At higher temperatures the theories tend to converge.

In conclusion, capillarity theories should neglect neither the mobility of the iron atom nor the atomic volume of the carbon atom. Trivedi and Pound (56) have shown that the atomic volume of carbon is of the same magnitude as iron, therefore it must not be neglected. Paxton and Pound have correctly included the driving force of the pure iron transformation but have incorrectly extrapolated the deviation from ideality to lower temperatures. This error is corrected for in
Figure 4.2. The capillarity constants of Friedel and Mullins (52), Hillert (7), Paxton and Pound (47), and Trivedi and Pound (56) are compared. Each constant is normalized with respect to that of Friedel and Mullins.
the present analysis by introducing the factor $B$, which is consistent with the statistical thermodynamic treatments of both KRC and ADP. Thus the interfacial concentrations accompanying ferritic precipitation from austenite are best described by this analysis.

Comparison of Theory and Experiment

Prediction of the edgewise growth velocity and tip radius is not possible from the theory unless the proper diffusivity is known and a reasonable interfacial energy and mobility can be estimated. The diffusivity of carbon in iron-carbon is understood to be a strong function of carbon concentration, however the solution to the diffusion equation was obtained assuming a constant diffusivity. If the diffusivity is a function of concentration, the diffusion equation becomes nonlinear, and its solution is only obtainable by numerical computer techniques. The nonlinear equation has been solved by Trivedi and Pound (53) and was found to be consistent with the linear equation if the constant diffusivity is assumed to be a diffusivity averaged over the concentration range present in front of the tip of the plate. Hence, the appropriate diffusivity is given by

\[
D = \frac{1}{C_i - C_\infty} \int_{C_i}^{C_\infty} D(c) dc ,
\]  

(4.9)

where $C_i$ and $C_\infty$ are austenitic concentrations at the interface and far from the interface, respectively. The diffusivity of carbon in austenite, $D(c)$, has been determined by Well, Batz, and Mehl (57)
over the concentration range up to 0.06 mole fraction carbon, where 
$D(c)$ was found to be

$$D(c) = D_0 e^{Ac}.$$  \hspace{1cm} (4.10)

$D_0$ is independent of concentration and is equal to $0.5 \exp(-38$ 
and $A$ is equal to $150,000/RT-30$. For a given temperature $\ln D(c)$ is 
a linear function of concentration up to 0.06 mole fraction. The 
present analysis predicts interfacial concentration as high as 0.09 
mole fraction carbon at $450^\circ C$, hence it was necessary to extend the 
observed linear dependence to 0.09 mole fraction carbon. The pos­
sibility of nonlinear behavior above 0.06 mole fraction was considered, 
and it was concluded that a reasonable nonlinear behavior would not 
change the interpretation of the transformation kinetics.

As mentioned in Chapter 11, the determination of a unique velocity 
and radius from the theory is not possible without involving an optimi­
zation principle. The present theory assumes that the precipitate in­
creases its length at a maximum rate. This assumption necessitated 
taking the partial of Equation 3.3 with respect to radius and setting 
$\delta W/\delta \rho = 0$ to obtain the maximum rate. When taking these partials, $D$ 
must be considered a function of radius. This results since $D$ is a 
function of interfacial concentration which in turn is dependent on 
the radius. If this is properly taken into account, Equation 3.7 must 
be modified; hence,
\[ 0 = \frac{Q_o}{2p} (2p + 1.0) - \frac{\Omega_o}{2\sqrt{\pi p}} e^{\text{erfc}(\sqrt{p})} + \sqrt{\pi p} e^{\text{erfc}(\sqrt{p})} \]
\[
\cdot \left[ \frac{V}{V_c} \frac{\rho_c}{\rho} s_1(p) + \frac{\rho_c}{\rho} s_2(p) - \frac{\rho_c}{\rho} \frac{s_2(p)}{(1 - \alpha)} - \frac{\rho_c}{\rho} s_1(p) \frac{\alpha}{(1 - \alpha)} \right], \quad (4.11)
\]

where
\[ \alpha = \rho \frac{\partial \ln D}{\partial \rho}. \quad (4.12) \]

In terms of the pertinent parameters,
\[ \alpha = f(p, \frac{\rho_c}{\rho}) = f(\Omega_o). \quad (4.13) \]

The dependence of \( \alpha \) on \( \Omega_o \) is shown in Figure 4.3. The assumption of \( D \) being independent of \( \rho \) is poorest for large values of \( \Omega_o \) and mobility. At 700°C, \( \Omega_o = 0.971 \), and infinite mobility the error in the predicted velocity is \(-3.58\%\); and the error in the predicted radius is \(+6.44\%\). In the worst possible case, the error is only a few percent. The inclusion of the alpha parameter in the theory greatly complicates the application of the theory and increases computer time while not improving its accuracy significantly. Hence, the diffusivity was assumed to be independent of radius throughout the analysis. It is noted, however, that this approximation may not be valid in other analysis where \( \Omega_o \) is extremely large.

The energy of the interface separating the matrix from the precipitate is also an influencing parameter in the theory. Although
Figure 4.3. The $\alpha$ parameter defined in Equation 4.12 is shown as a function of normalized supersaturation. The parameter $Q$ is $\mu_o (c_o - c_\infty) \rho_C / 2 \bar{U}$. 
estimates of its magnitude have been made, the actual interfacial energy is obtained from the comparison of the theory with the experimental data. The energy of a semicoherent martensitic interface has been estimated (58) to be about 200 ergs/cm$^2$, which sets a lower limit for a reasonable interfacial energy. An upper limit would be about 800 ergs/cm$^2$, which corresponds to a highly disordered interface. Thus, independent experimental data restricts a reasonable prediction of interfacial energy to this range.

The value of the interfacial kinetic parameter, $\mu_o$, also is not known from independent experiments. This too is adjusted to make the theory and experimental data consistent with each other. The credibility of the magnitude of $\mu_o$ can be checked by comparing it with kinetic data from interfacial migration during grain growth and the massive transformation in other systems. Also, the predicted interface kinetic parameter can be related to the grain boundary diffusivity, offering an additional check on the reasonable nature of $\mu_o$.

Hence in review, independent experiments provide the needed information concerning equilibrium interfacial concentrations and their dependence on curvature. In addition, the solute diffusivity is measured independently. Although the magnitude of the interfacial energy and the interfacial kinetic parameter can be estimated qualitatively, their exact values must be determined from a comparison of the theory with Widmanstätten kinetic and tip radii data.

Equations 3.3 and 3.7 can now be used to calculate the lengthening kinetics and radii for assumed values of interfacial energy.
and kinetics parameter. In the initial comparison between theory and experiment, the interfacial kinetics were assumed to be infinite. Under the assumption of infinite interface kinetics the predicted and measured kinetics are shown in Figure 4.4 for the limiting range of reasonable interfacial energies, 200 and 800 ergs/cm$^2$. Neither extreme interfacial energy describes the kinetics over the entire temperature range. An interfacial energy of 200 ergs/cm$^2$ fits the data well at 700°C but predicts kinetics an order of magnitude too fast at 450°C. An interfacial energy of 800 ergs/cm$^2$ fits the data at 650 and 550°C but is in error at 700 and 450°C. If the nature, i.e., coherency, of the interface is independent of temperature, then the interfacial energy likewise will be essentially independent of temperature. Thus, the kinetics over the entire temperature range cannot be rationalized without including the effect of interfacial kinetics.

The inclusion of an interfacial kinetic effect retards the kinetics. Figure 4.4 shows that even for infinite kinetics, 200 ergs/cm$^2$ is the largest interfacial energy that is consistent with the measured kinetics. To rationalize the data at 700°C, the interfacial kinetics have to be essentially infinite and the interfacial energy has to be 200 ergs/cm$^2$. Thus, it is predicted from the kinetics that the interface has a semicoherent structure. In addition, a comparison of the measured and predicted radii indicates the interfacial energy must be less than 650 ergs/cm$^2$. This result follows since $\sigma_c \leq \frac{1}{2} \rho$ (experimental). Thus a complete disordered interfacial boundary can be considered implausible. Henceforth, it is concluded that the
Figure 4.4. Velocity versus supersaturation for infinite interfacial kinetics and interfacial energies of 200 ergs/cm$^2$ and 800 ergs/cm$^2$. 
interfacial energy is 200 ergs/cm^2 at all temperatures. The discrepancy between the measured and predicted values at lower temperatures is assumed to be due to the presence of an interfacial kinetic effect.

Figure 4.5 shows the agreement between the measured and predicted kinetics if the interface kinetics are assumed to be finite. The predicted kinetic parameters are shown in Table 6 as a function of temperature. It is of interest to transform the kinetic parameter into a more meaningful interfacial mobility, M. This facilitates the comparison of the predicted interfacial kinetics with independent experimental data concerning interfacial migration.

The theory assumes that the interfacial velocity is proportional to a deviation from equilibrium across the interface in terms of concentration, thus

\[ V = \mu_0 \Delta C_K \]  \hspace{1cm} (4.14)

where \( \Delta C_K = C - C^* \). It is more physically meaningful, however, to consider the mobility of the interface whose definition assumes that the interface moves at a rate proportional to the free energy gradient across the interface according to the relationship,

\[ V = M \frac{\Delta G_K}{\delta} \]  \hspace{1cm} (4.15)

It is assumed that \( \Delta G_K << R\bar{T} \), where \( \Delta G_K \) is the free energy difference across the interface; and \( \delta \) is the interfacial thickness. The \( \Delta G_K \)
Figure 4.5. Velocity versus supersaturation is shown for finite interfacial kinetics and an assumed interfacial energy of 200 ergs/cm². The error limits indicate 50% confidence.
Table 6. The interfacial kinetic parameter, $\mu_0$, and the interfacial mobility, $M$, are shown as a function of temperature for the thermodynamic extrapolations of KRC (46) and ADP (50).

<table>
<thead>
<tr>
<th>Temperature $^\circ$C</th>
<th>$\mu_0$ (ADP) cm/sec-mole fraction</th>
<th>$M x 10^2$ $^2$ cm/sec-cal</th>
</tr>
</thead>
<tbody>
<tr>
<td>700</td>
<td>0.60</td>
<td>7.20</td>
</tr>
<tr>
<td>650</td>
<td>0.30</td>
<td>3.10</td>
</tr>
<tr>
<td>550</td>
<td>0.09</td>
<td>0.75</td>
</tr>
<tr>
<td>450</td>
<td>0.07</td>
<td>0.84</td>
</tr>
</tbody>
</table>
is the free energy necessary to transport the iron and carbon atoms across the interface at a rate \( v \). Equations 4.14 and 4.15 can be combined to obtain a relationship between interfacial mobility and the interfacial kinetic parameter as follows,

\[
M = \mu_0 \frac{\Delta C_K}{\Delta G_K} .
\]  

(4.16)

The same thermodynamic expressions as were utilized in the capillarity calculations were used to convert \( \Delta C_K \) to the corresponding \( \Delta G_K \). The calculated mobilities are shown in Table 6. The curves plotted in Figure 4.5 are for a constant mobility at each temperature. Although in practice it is more convenient to keep the kinetic parameter independent of driving force, it is more realistic to assume the mobility to be independent of driving force. The mobilities calculated in Table 6 are calculated under the assumption that the carbon atom is infinitely mobile, such that the predicted interfacial mobility \( M \) is actually the mobility of the iron atom as it crosses the interface. Later, it will be shown that the predicted interfacial mobilities are correct even if this assumption is not valid.

In addition to the lengthening kinetics, the theory also predicts the tip radius. Experimental tip radii have been reported by Simonen, Aaronson, and Trivedi (41) and are shown in Table 7. The radii are determined from the maxima in frequency histograms constructed from 50-100 measurements. Typical histograms are shown in Figure 4.6. The discontinuities in the data are smoothed in Figure 4.7 to delineate
Table 7. Experimental radii of curvature for Widmanstätten ferrite are shown as a function of temperature and composition

<table>
<thead>
<tr>
<th>T°C</th>
<th>0.24% C</th>
<th>0.33% C</th>
<th>0.43% C</th>
</tr>
</thead>
<tbody>
<tr>
<td>750</td>
<td>180</td>
<td></td>
<td></td>
</tr>
<tr>
<td>725</td>
<td>165</td>
<td>230</td>
<td></td>
</tr>
<tr>
<td>700</td>
<td>95</td>
<td>155</td>
<td>180</td>
</tr>
<tr>
<td>600</td>
<td>75</td>
<td></td>
<td></td>
</tr>
<tr>
<td>550</td>
<td>65</td>
<td>120</td>
<td>70</td>
</tr>
<tr>
<td>500</td>
<td>60</td>
<td></td>
<td></td>
</tr>
<tr>
<td>360</td>
<td>65</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Figure 4.6. Frequency histograms of the radii of curvature data in the 0.24% C alloy at the indicated reaction temperatures.
Smooth curves drawn through the histograms shown in Figure 4.6. The three curves are superimposed to illustrate the effect of temperature on the histogram shape.
the decreasing breadth of the maxima with decreasing temperature. Yost and Trivedi (59) have shown that this result is consistent with the determination of the rate of lengthening by the maximum growth rate principle. The experimental and theoretical radii are compared in Figure 4.8, where the theoretical assumptions are identical to those made in the kinetic analysis shown in Figure 4.5. The conclusion is drawn that the model is consistent with the observed tip radii.

Partitioning of Supersaturation

The total supersaturation available to drive the transformation is dictated by the alloy composition, $C_0$, and the alloy phase diagram, i.e., $C_o$ and $C_p$. The supersaturation is divided between three competing physical processes; namely, volume diffusion, interfacial creation, and interfacial mobility. Partitioning of the free energy of transformation into these processes can be easily seen by the use of the free energy diagram shown in Figure 4.9. The dotted curved represents the case of a flat interface. It has been assumed in the capillary consideration that the capillary effect changes the free energy of the precipitate only, which follows the convention given by Hillert (7). For the sake of clarity the changes in precipitate concentration are not shown. The free energy dissipated by volume diffusion, interfacial kinetics, and capillarity are shown as $\Delta G_d$, $\Delta G_k$, and $\Delta G_c$, respectively.

Equation 3.3 is in a form which shows how the total supersaturation is divided. The first term, second term, and third term represent
Figure 4.8. The measured radii of Widmanstätten ferrite are compared with the predictions of the theory.
Figure 4.9. Free energy dissipated by diffusion, kinetics, and capillarity
the supersaturation dissipated by volume diffusion, interfacial kinetics, and capillarity, respectively. The partitioning at 700°C as a function of supersaturation, \( (C_0 - C_\infty) \), is shown in Figure 4.10. It is observed that for larger driving forces diffusion and interfacial mobility consume a greater share of the supersaturation at the expense of capillarity. Diffusion demands by far the greatest part of the total driving force with a significant portion being consumed by capillarity at low supersaturations. A similar plot for the partitioning of supersaturation for the Fe-24% C alloys as a function of temperature is also shown in Figure 4.10. It is again observed that for increasing driving force (decreasing temperature) capillarity consumes less of the available energy, whereas interfacial kinetics consumes a slightly larger fraction. The observation that capillarity consumes a smaller fraction of the supersaturation for larger driving forces is consistent with the capillarity analysis shown earlier. It was shown that the predictions of Paxton and Pound were qualitatively correct. In their analysis the capillary term, \( \Gamma \), is inversely proportional to the total driving force for the transformation in pure iron, such that a larger driving force reduces the capillarity effect. This is exactly the dependence observed in Figure 4.10. This behavior indicates that errors in the capillarity assumptions would be reflected in the predictions to a greater extent for low supersaturations and the assumptions in the volume diffusion analysis would be reflected to a greater extent for high supersaturations. It is of interest to note that these results differ from the predictions of the Zener-Hillert equation,
Figure 4.10. Partitioning of the normalized supersaturation
which always partitions the driving force evenly between capillarity and volume diffusion.

The phase diagram shown in Figure 4.11 shows the driving force \( \Delta C_K \) and \( \Delta C_C \) consumed by kinetics and capillarity, respectively, for the Fe-.24% C alloy. The interface concentration is seen to be an approximate linear function of temperature given by

\[
C_t = 0.23 - 0.0002 T .
\]

(4.17)

The significance of the predicted interfacial mobility, \( M \), will now be considered. As mentioned earlier, the mobility was calculated under the assumption that the carbon could cross the interface virtually at an infinite rate. Although this assumption was made, it does not affect the result in the present system. This can be seen from the free energy diagram in Figure 4.12, where the effect of curvature has been corrected for. \( \tilde{\nu}_{P_t} \) and \( \tilde{\nu}_{P_\rho} \) are the precipitate concentrations at the tip and the equilibrium precipitate concentration, respectively. The free energies, \( \Delta G_{K,Fc} \) and \( \Delta G_{K,C} \), represent the difference in free energy of iron and carbon across the interface. It is seen from both free energy diagrams that if the precipitate concentration is nearly zero, as is the case, \( \Delta G_{K,Fc} \) is essentially equal to \( \Delta G_{K,C} \) for the interface. The effect of \( \Delta G_{K,C} \) is not significant.

In order to calculate the interfacial mobility, \( M \), from Equation 4.16, the values of \( \Delta G_K \) must be calculated from \( \Delta C_K \) predicted by the theory. Deviations from equilibrium in terms of
Figure 4.11. Iron-carbon phase diagram in the region of interest. $\Delta C_K$ and $\Delta C_C$ are the kinetic and capillarity shifts predicted by the model.
Figure 4.12. $\Delta G_{K,Fe}$ and $\Delta G_{K,C}$ represent the chemical potential gradient across the austenite-ferrite interface for iron and carbon.
concentrations must be transformed into deviations from equilibrium in terms of free energy or chemical potential. The deviation of chemical potential of iron across the interface is given by the relationship

\[ \Delta G_{Fe} = \Delta G_{Fe,\gamma} - \Delta G_{Fe,\alpha} \]  

(4.18)

where \( \Delta G_{Fe,\gamma} \) and \( \Delta G_{Fe,\alpha} \) are deviations in chemical potential from equilibrium values in \( \gamma \) and \( \alpha \) phases, respectively.

From the thermodynamic relationships (46), we obtain

\[ \Delta G_{Fe,\gamma} = \frac{RT}{5} \ln \left[ \frac{(1-C_p)^{1-C_t}}{1-C_p(1-C_t)} \right] \]  

(4.19)

and

\[ \Delta G_{Fe,\alpha} = RT \ln \left[ \frac{1-C_p}{1-C_p} \right] \]  

(4.20)

Since the precipitate concentration is virtually zero, the expression for \( \Delta G_{Fe,\alpha} \) vanishes from Equation 4.18. It follows that the chemical potential of iron across the interface is

\[ \Delta G_{Fe} = \frac{RT}{5} \ln \left[ \frac{(1-C_p)}{(1-C_p)} \cdot \frac{(1-C_t)}{(1-C_t)} \right] \]  

(4.21)

Likewise, the chemical potential difference of carbon across the
interface is given by the relationship

\[ \Delta G_C = RT \ln \left[ \frac{(1-6C_p)}{(1-6C_p)} \frac{C_p C_p, t}{C_t, C_{p, o}} \right] . \] (4.22)

The free energy, \( \Delta G_K \), dissipated at the interface, is equal to the free energy liberated by an interfacial process when one mole of ferrite is formed. This is given by

\[ \Delta G_K = (1-C_p, t) \Delta G_{Fe} + C_p, t \Delta G_C . \] (4.23)

Since \( C_{p, t} \) is almost zero, the order of \( 10^{-3} \) mole fraction, then

\[ \Delta G_K = \Delta G_{Fe} . \] (4.24)

Therefore,

\[ \Delta G_K \approx \frac{RT}{5} \ln \left[ \frac{(1-6C_p)}{(1-C_p)} \left( \frac{1-C_p}{1-6C_p} \right) \right] . \] (4.25)

Thus from Equations 4.15 and 4.25 the following relationship between \( M \) and \( \mu_0 \) is obtained

\[ M = \frac{5 \gamma}{RT} \left[ \ln \left( \frac{1-6C_p}{1-C_p} \right) -1 \right] \] (4.26)

The above expression was utilized to calculate the values of
interfacial mobility from the predicted interfacial kinetic parameters shown in Table 6.

Interpretation of $M$

As shown earlier, the interfacial mobility, $M$, in the case of ferrite growing from austenite corresponds to the mobility of the iron atoms as they cross the interface. Consequently, the magnitude of the predicted interfacial mobility should be comparable to the expected mobility of iron as determined from grain boundary diffusion data, if the atoms transfer across the interface independently. Atomistically, the mobility of an interface moving by a thermally activated process of atomic jumps can be expressed as

$$M = \gamma f \frac{2}{\gamma f} \exp\left(-\frac{\Delta G_m}{RT}\right) = \frac{D_m}{RT} ,$$

(4.27)

where $1/f$ is the number of jumps that is necessary before an atom of austenite permanently settles in a ferritic site. Gamma is the areal fraction of sites at the ferritic interface which can accept the migrating atom. The activation energy for a single jump is $\Delta G_m$, and $\nu$ is the atomic vibrational frequency. $D_m$ is the diffusivity for interfacial migration, which in this case is related to the grain boundary diffusivity of iron. The boundary mobility is related to iron grain boundary mobility by

$$M = \gamma f M_{Fe} .$$

(4.28)
Thus the two are identical if an iron atom can transfer from the austenite to the ferrite in one jump and if all interfacial sites in the ferrite can accommodate the transferring atom.

A plot of $M$ versus $1/RT$ predicts both the activation energy for migration from the slope and the pre-exponential coefficient, including the product $\gamma_f$ from the intercept. Figure 4.13 shows the plot for the phase boundary extrapolation of ADP and KRC. The activation energies and intercept data from Table 8 for ADP presage the $\gamma_f$ product to be about 35 if $\nu = 10^{12}$ sec$^{-1}$, $\sigma = 3 \times 10^{-8}$ cm, and an intermediate temperature of 550°C. Thus, if an atom makes ten jumps to cross the interface, then about one third of the sites in the ferrite can accommodate the migrating atom. The magnitude of the intercept is in excellent agreement with this boundary migration model.

The magnitude of the austenite-ferrite interfacial mobility was compared with an experimentally determined interfacial mobility (60) for the beta to alpha massive transformation in copper-zinc alloys at a homologous temperature. The comparison indicates that the predicted iron-carbon boundary is about one order of magnitude less mobile than the massive interface. This result supports the conclusion that the magnitude of the determined Widmanstätten interfacial mobility is not highly unreasonable.

The predicted activation energies are, however, much lower than expected from grain boundary diffusion data in pure iron. The activation energy for grain boundary diffusion of iron in pure iron is expected to be approximately 40 Kcal (61), more than double the energy
Figure 4.13. The mobility predictions obtained from KRC thermodynamics (•) and ADP thermodynamics (o) are plotted versus reciprocal temperature.
Table 8. The dependence of the iron-carbon phase boundary extrapolation on the interfacial mobility intercept and activation energy is shown.

<table>
<thead>
<tr>
<th>Phase Boundary Extrapolation</th>
<th>$Q_M$ (Kcal/mole)</th>
<th>Intercept (cm/sec-cal)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ADP (50)</td>
<td>15.3 ± 2.5</td>
<td>$1.6 \times 10^{-8}$</td>
</tr>
<tr>
<td>KRC (46)</td>
<td>11.8 ± 3.2</td>
<td>$2.2 \times 10^{-7}$</td>
</tr>
</tbody>
</table>
predicted by the present data. Initially, this may seem to destroy the plausibility of the assumption of the interfacial migration to be a thermally activated process. However, a more thorough investigation indicates that it is expected that the activation energy would be considerably less than that for grain boundary diffusion in pure iron. This is because the self-diffusion of iron appears to be a strong function of carbon content. The results of Wells, Batz, and Mehl (57) are consistent with the notion that the presence of carbon weakens the atomic bonding in austenite and enhances the diffusivity. Gruzin (62) has measured the self-diffusion of iron in austenite as a function of carbon content and has found that the diffusivity is enhanced by the presence of carbon. The self-diffusion coefficient if iron in austenite is given by

$$D_{Fe}^{\gamma} = 10^{-c} \exp\left(-\frac{69,000 - 7,000 c}{RT}\right),$$  \hspace{1cm} (4.29)

where \(c\) is atom percent carbon. In this case it is not known whether the effect of carbon is primarily in changing the vacancy formation energy or in changing the energy for migration. If the activation energy for iron migration in austenite is reduced by the presence of carbon, the boundary activation energy could also be influenced by the presence of carbon. Hence, the possibility of the boundary migrational activation energy being a function of carbon content needs to be explored.
To estimate the possible influence of carbon, it is assumed that the activation energy for grain boundary self-diffusion is one half that for bulk self-diffusion and that the pre-exponential coefficient for grain boundary self-diffusion is proportional to that for bulk diffusion. These assumptions permit the following expression for $D^B_{Fe}$, the boundary self-diffusivity of iron,

$$D^B_{Fe} = \beta 10^{-c} \exp\left(-\frac{(69,000 - 7,000 c)}{2RT}\right),$$

where $\beta$ is a constant. In Figure 4.14 this coefficient is compared with the predicted coefficient from the Widmanstätten kinetic data for the case of beta equal to five. The agreement is remarkably good and suggests the plausibility of the above discussion. The predicted small activation energy from the kinetic data could be a result of the presence of carbon. In any case, the presence of carbon and the fact that the interfacial concentration is a function of temperature casts serious doubt on any apparent activation energy that is obtained from a $\ln D^B_{Fe}$ versus $1/RT$ plot.

Guiraldenq and Lacombe (61) have measured grain boundary self-diffusion of iron in austenite and ferrite. The predicted values from this treatment are much faster than those measured in pure iron. Intuitively it is often thought that the short range migration of iron across the interface would be much greater than the long range migration of carbon in the bulk. Thus, it usually is expected that the short range diffusion of iron would be so rapid that it would not affect the
Figure 4.14. The interfacial mobility is plotted versus reciprocal temperature. The kinetic prediction is obtained from Figure 4.13 and the diffusion prediction is obtained from Equation 4.30.
kinetics. The present analysis has shown that the short range diffusion of iron can markedly influence the kinetics even for assumed values more rapid than expected from grain boundary diffusion data in pure iron.

It has been shown that if local equilibrium is assumed to prevail at the interface as Widmanstätten ferrite precipitates from austenite, then the lengthening kinetics of these plates are not rationalized by volume diffusion control. It was necessary to assume a deviation from local equilibrium at the interface. This deviation was considered to be necessary to drive the short range diffusion of iron across the interface. The predicted rate of diffusion was correlated with the expected boundary self-diffusivity of iron as measured by independent experiments. The comparison was good and not inconsistent with the assumption that the interface advances at a rate partially determined by the rate of independent migration of iron atoms across the interface. This rate is in agreement with the model presented for an interface moving at a determined rate by a thermally activated process, which in this case is the short range diffusion of iron.

Hillert's Interpretation of the Deviation from Equilibrium

Hillert (40) has suggested a different type of resistance to interfacial motion which is independent of interfacial velocity. He has propounded a barrier for growth which must be overcome but once overcome offers no further resistance. The resistance is analogous
to a static coefficient of friction which must be overcome to initiate motion. In the present case, the analogous kinetic coefficient of friction is assumed to be nonexistent. An example of a cause for such interfacial resistance is an array of pinning points which prohibit interfacial motion, but when overcome are no longer effective in disturbing the movement of the interface. If it is assumed that the resistance acts with equal strength at all portions of the interface, edge and sides alike, then the kinetic predictions are obtained as shown in Figure 4.1. $\Delta C_K$ now represents the supersaturation needed to initiate interfacial motion. The resistance to interfacial motion may be due to a pinning phenomena, interfacial coherency, transformation strains, or some undetermined thermodynamic effect.

The $\Delta C_K$ illustrated in the phase diagram in Figure 4.11 corresponds to the driving force lost in this type of interfacial resistance. The theory predicts that the same energy is lost whether it be in interfacial migration processes or a process needed to initiate interfacial motion as suggested by Hillert. Thus it is not possible from the Widmanstätten kinetic data alone to predict the details of the dissipative process which is apparently consuming energy at the interface. To obtain a more complete understanding, it is necessary to look toward kinetics of other transformations in the iron-carbon system; namely, grain boundary ferrite, upper bainite, and lower bainite. From a kinetic interpretation of these transformation, the evidence suggests that the arguments of Hillert possess more credibility. Hence, thermodynamics, as intimated by Hillert, appears to be most likely responsible
Figure 4.15. Edgewise growth rate is shown as a function of driving force for a finite shift in the phase diagram, $\Delta C_K$, as suggested by Hillert (40).
for the predicted deviation from equilibrium rather than the kinetic effect previously described. This conclusion is based, however, on data from other transformations and further discussion will be postponed until these transformations are considered in detail in Chapter VI.
CHAPTER V: WIDMANSTÄTTERN GROWTH IN ALPHA-BETA BRASS

General Characteristics

The surface relief and diffusional characteristics of the Widmanstätten transformation are manifested when alpha plates and needles precipitate from beta brass. Garwood (63) in 1954 was the first to study the transformation with an intent to discover the transformation mechanism. He observed that the plates form with certain martensitic characteristics such as habit plane, internal stacking faults, and a surface relief. The conclusion was drawn that the argument of Ko and Cottrell (45) was applicable to this transformation. The argument states that the atoms are transformed from one phase to the other by a cooperative martensitic-like shear, whereas the slow kinetics are limited by atomic diffusion. From a determined activation energy for the incubation period, Garwood suggested that diffusion takes place inside the precipitate. Because of the appearance of a surface relief and the slow diffusion limited kinetics, the transformation has been classified as a bainitic transformation; although the precipitate structure is single phase as opposed to the duplex structure of bainite in steels.

More recently a number of investigators have studied and reported considerable data on the morphology, orientation, precipitate stacking faults, and the kinetics of the beta to alpha transformation. This renewed interest was reviewed at the symposium on the Physical Properties of Martensite and Bainite (24) in 1965. The main points relating to the transformation brought out at this time were its close relationship to
subzero martensite and the morphological transition from plate to needle with increasing temperature and decreasing supersaturation. T-T-T diagrams were established for plate and needle formation, and it was found that separate C curves are manifested by each morphology. The nucleation kinetics were thus established as being different for the plate and the needle. An upper temperature limit for plate formation was observed metallographically and was found to be parallel to the martensite $M_S$ temperature as a function of composition. Repas and Hehemann (20) measured the upper temperature limit for plates by recording their existence from observations of stacking faults. The faults are present in plates but not in needles, and hence serve as a criteria for distinguishing between the two morphologies. The stacking fault results indicate that the upper temperature limit does not parallel the martensite $M_S$ temperature.

It has been postulated (64) that the nucleation event could be induced by the motion of partial dislocations on $\{110\}_B$ planes, which closely brings a bcc atomic arrangement into coincidence with a fcc structure. Head et al. (65) have observed that 90% of all dislocations in beta brass are pure screw and are oriented in the $\langle 111 \rangle_B$ direction. The orientation of the needle axis is also close to this direction, hence nucleation may take place on these dislocations. It seems likely that dislocations play a vital role during the nucleation event. The morphological transition may be reflecting differences in nucleation characteristics as opposed to growth characteristics.
The crystallography of the transformation has been determined. Although it does not enter the present model for edgewise growth kinetics, it is perhaps worthwhile to present these results. The needle-shaped precipitates have their axis along \( \langle 556 \rangle_B \), whereas the plates exhibit a habit plane of \( \{2,11,12\}_B \) (20). Recent evidence (66) has revealed an addition habit plane near \( \{1,2,3\}_B \). The orientation relationship between the two phases is within a few degrees of \( \{111\}_B \parallel \{110\}_\alpha \), \( \langle 110 \rangle_B \parallel \langle 111 \rangle_\alpha \), the Kurjumov-Sachs orientation. This relationship is the same as is observed for the Widmanstätten ferrite-austenite interface in steel. The crystal structure of the needle precipitate is believed to be fcc, whereas the plate precipitate is reported to be either faulted fcc or fct.

The precipitate concentration has been measured for both the needle and plate shapes (67), thus providing empirical proof that the transformation is indeed accompanied by solute partitioning. The assumption that volume diffusion plays an important role in influencing the kinetics is thus justified. The results indicate that the precipitate concentration is near equilibrium for needle growth at 500°C but deviates from equilibrium for plate growth at lower temperatures.

Repas and Hehemann (20) have measured the edgewise growth kinetics of alpha plates and needles over a range of compositions and temperatures. They found that the data did not indicate any discontinuity in the kinetic behavior as the alloy composition was varied from the plate region to the needle region of the phase diagram. This is in contrast to the nucleation behavior of Flewitt and Towner (67), which
did show a discontinuity. The portion of the Cu-Zn phase diagram of interest is shown in Figure 5.1. The upper temperature limit for plate formation, the plate start temperature, is indicated on the diagram. Repas and Hehemann compared their data with a Zener-Hillert model and found the experimental kinetics to be more rapid than predicted.

Purdy (42) has measured the tip radii and lengthening rate of alpha needles in two alloys at 400°C with scanning electron microscopy. The results were compared with the theory of Trivedi (10), and it was concluded that the observed kinetics and radii were in agreement with equilibrium thermodynamics and volume diffusion for an interfacial energy of 500 ergs/cm$^2$. This suggested that the tip interface is disordered and different in nature from the semicoherent Widmanstätten ferrite tip interface. It is the intent of this thesis to challenge this conclusion by providing evidence to support the notion that the tip interface is semicoherent. Purdy has rationalized the apparent kinetic discrepancy between theory and experiment by attributing it to the nonideality of the alpha and beta solid solutions.

The bainitic plates and needles in brass are seen to possess many characteristics similar to bainite and Widmanstätten ferrite in steels with respect to morphology, interfacial orientation, surface relief, and solute partitioning. It is, thus, advantageous to compare their kinetic behavior with the present growth model to aid in the development of a general model of Widmanstätten precipitation. The model can only be realized if proper consideration is given to interfacial creation,
Figure 5.1. The Cu-Zn phase diagram is shown in the region of interest. The plate start temperature is the upper temperature limit for plate formation.
volume diffusion, and deviation from equilibrium. The following discus­sion presents these considerations and relates them to the general model.

Creation of an Alpha-Beta Interface

The effect that interfacial creation has on the kinetics of phase transformations is dependent upon the thermodynamics of the phases involved. Thermodynamic data indicate that the alpha and beta solid solutions are not ideal solutions; hence, it is necessary to derive expressions for the dependence of equilibrium concentration on interfacial curvature, which is also known as the effect of capillarity. Purdy (42) has stressed the importance of nonideality for the growth of alpha needles from beta brass. His result is given below

\[ c_\rho = c_\alpha \left[ 1 + \frac{1-c_\alpha}{c_\rho - c_\alpha} \frac{2\sigma V}{\rho RT e_B} \right] \]  

(5.1)

where \( e_B \) is the nonideal thermodynamic parameter and the other parameters have their usual meanings. A similar expression exists for the alpha phase. Repas and Hehemann have derived the same expression for the assumption of ideal solution, where \( e_B \) is unity. The development of the above expression assumes that the difference between the interfacial concentration for the flat and curved interface is small. To determine the magnitude of the error associated with this assumption a more rigorous numerical solution to the problem is obtained.
Utilizing a procedure similar to that used for Fe-C, the difference in the concentration dependent chemical potential of the atoms across the interface is set equal to the capillarity term, \( \sigma \bar{V}/\rho \), where \( \bar{V} \) is either the atomic volume of the copper, \( \bar{V}_{Cu} \), or the atomic volume of zinc, \( \bar{V}_{Zn} \). The atomic volumes were assumed to be equal to 7.8 for the present calculations. Thus, in terms of chemical potentials, \( \bar{G} \),

\[
\bar{G}_{Cu,\alpha} - \bar{G}_{Cu,\beta} + \sigma \frac{\bar{V}_{Cu}}{\rho} = 0 \tag{5.2}
\]

\[
\bar{G}_{Zn,\alpha} - \bar{G}_{Zn,\beta} + \sigma \frac{\bar{V}_{Zn}}{\rho} = 0 \tag{5.3}
\]

where one obtains from Hultgren et al. (68)

\[
\bar{G}_{Cu,\alpha} = G_{Cu,\text{fcc}} - 3160 \frac{c^\alpha}{(1 - c^\alpha)^2} + RT \ln(1 - c^\alpha) \tag{5.4}
\]

\[
\bar{G}_{Zn,\alpha} = G_{Zn,\text{solid}} - 6490 + 6320 \frac{c^\alpha}{1 - c^\alpha} + RT \ln c^\alpha \tag{5.5}
\]

\[
\bar{G}_{Cu,\beta} = G_{Cu,\text{fcc}} - 10520 \frac{c^\beta}{c^\beta} + 1030 + RT \ln(1 - c^\beta) \tag{5.6}
\]

\[
\bar{G}_{Zn,\beta} = G_{Zn,\text{solid}} - 10520(1 - c^\beta)^2 + 490 + RT \ln c^\beta \tag{5.7}
\]

Substitution of Equation 5.4 - 5.7 into Equations 5.2 and 5.3 yields
Equations 5.8 and 5.9 represent two transcendental relationships involving two variables \(c^\alpha_0\) and \(c^\beta_0\). The solution to these relationships was obtained numerically on a digital computer.

A comparison between these exact results and those derived with Purdy's approximation, Equation 5.1, are shown in Figure 5.1. The excellent agreement indicates that the assumptions of Purdy's expression are valid and his approximate relationship is correct for the present analysis. The numerical value of \(e_\beta\) is calculated from the definition of \(e_\beta\) and from the data of Hultgren et al. (68) Purdy has reported that the nonideal parameter is equal to 13. The same calculation has been repeated in the present work and the value of \(e_\beta\) was found to be 4.41. The approximate result shown in Figure 5.2 is made for \(e_\beta\) equal to 4.41 and is seen to be consistent with the rigorous capillarity predictions made from Equation 5.8 and 5.9. Since a nonideal parameter of 13 is inconsistent with the rigorous treatment, it is concluded
Figure 5.2. The beta equilibrium concentration at a curved alpha-beta interface is shown as a function of curvature. The approximate results are obtained from Equation 5.1 for $e_B$ equal to 4.41. The exact solution represents the solution to Equations 5.8 and 5.9.
that Purdy's calculation is in error. The calculation of $e_B$ is performed in the Appendix. The difference in calculated values is important since the erroneous value predicts kinetics one order of magnitude faster than the correct value. The calculations were made on the basis of thermodynamic data taken at 500°C. In the interpretation of the kinetic data, it will be necessary to consider that the nonideality may vary with temperature as is the case for iron-carbon austenite.

**Edgewise Growth Kinetics of Alpha Precipitates in Beta Brass**

The edgewise growth kinetics of alpha needles and alpha plates were calculated under the assumption of equilibrium thermodynamics and volume diffusion as the partitioning mechanism. The predictions are shown with the experimental results in Figures 5.3 and 5.4. The needle growth rate reported in Figure 2.9 is not included in the analysis because the measurement was inconsistent with the rest of the data, and chemical analysis indicated that the alloy lost one percent zinc during the specimen preparation. It was concluded that the result was spurious. The experimental data points shown in Figures 5.3 and 5.4 are taken from Tables 4 and 5.

The theoretical predictions were made for an assumed interfacial energy of 200 ergs/cm². This is the smallest value that could be assumed to bring the theoretical and experimental data into agreement. Larger energies create a larger discrepancy, whereas smaller energies are unrealistic. The flat interfacial equilibrium concentrations were
Figure 5.3. Needle kinetics for equilibrium and $\sigma = 200 \text{ ergs/cm}^2$
Figure 5.4. Plate kinetics for equilibrium and $\sigma = 200$ ergs/cm$^2$
determined from the phase diagram shown in Figure 5.1. The chemical interdiffusion constant was calculated from the diffusion data of Kuper et al. (69) and the thermodynamic data of Hultgren et al. (68). It is seen that the measured kinetics are more rapid than predicted, and the discrepancy becomes greater with decreasing temperature. Possible explanations for the observed enhanced kinetics will now be discussed in terms of interfacial creation, enhanced diffusivity, and deviation from equilibrium. In particular, deviation from equilibrium in the precipitate is concluded to be the primary cause for the kinetic discrepancy between experiment and the model.

If it is assumed that the model is in basis correct, then the above kinetic discrepancy must be attributed to an incorrect application of an assumption concerning interfacial creation, diffusivity, or equilibrium. There are two basic assumptions that pertain to interfacial creation, which may be a source of error in the model. The first assumption is that the nonideal solution parameter, which enters the capillarity calculation, is independent of temperature. The second uncertain assumption relates to the interpretation of the predicted interfacial energy.

Throughout the kinetic and capillarity analyses, it has been assumed that both solid solutions, alpha and beta, are regular solutions; hence, it was assumed that the nonideal parameter does not vary with temperature. The parameter was calculated on the basis of thermodynamic data taken at 500°C, then used over the entire temperature range of the experimental data. The same parameter was calculated on
the basis of thermodynamic data taken at 723°C and was found to be less than the lower temperature calculation. This indicates that the two solid solutions are not regular and thus the parameter does vary with temperature. If the nonideal thermodynamic parameter is allowed to vary to fit the kinetic data, then it must depend on temperature as shown in Figure 5.5 as a dashed line below 500°C. It is predicted that the beta solution becomes less ideal with decreasing temperatures. This is consistent with the data points calculated on a thermodynamic basis at 500°C and 723°C.

It should be noted that the influence of nonideal solution behavior also affects the magnitude of the diffusivity used in the theory. The diffusion data given by Kuper et al. (69) pertains to tracer diffusion, which must be multiplied by $e^B$ to obtain the chemical interdiffusivity used in the present model. Hence, the predicted kinetics are proportional to the nonideal parameter squared. Both the capillarity and diffusivity effects are included in the predicted extrapolation shown in Figure 5.5.

It is seen that nonideality enters the capillarity calculation in brass as it did in steel. In brass the effect is included in the capillarity relationship, Equation 5.1, by introducing the parameter $e_B^2$, whereas in steel the effect is included by using the empirical parameter, $B$, in Equation 4.8. The cases of $B$ equal to zero and $e_B$ equal to one correspond to ideal solution behavior.

The second uncertain assumption that pertains to interfacial creation is the assumed dependence of capillarity on interfacial energy.
Figure 5.5. The nonideal parameter, $\theta_B$, is plotted versus temperature. The dashed line is chosen to match the needle kinetics. The experimental points are calculated from Hultgren et al. (68)
and curvature. Good agreement results in both the kinetics and radii if the apparent interfacial energy is allowed to take on values as low as 50 ergs/cm$^2$. The apparent interfacial energy may be much less than expected due to the atomistic nature of the interface. This implies that the nature of interfacial ledges and ledge-ledge interactions may affect the interfacial creation and capillarity in such a fashion that the manifested interfacial energy is less than expected. Interfacial curvature hinders growth when that growth is accompanied by an increase in interfacial area. However, the resistance to growth would be less if the growth were also accompanied by a decrease in ledge-ledge interactions. The interfacial energy predicted by the theory may be composed of many effects other than interfacial creation. If so, the interpretation of the magnitude of the interfacial energy should include these effects. It is possible that the predicted interfacial energy of 50 ergs/cm$^2$ for needle growth at 250°C may have a physical but cryptic meaning.

Thus, the enhanced experimental edgewise growth kinetics of alpha precipitates in beta brass can be interpreted in terms of two uncertain approximations relating to interfacial creation. As is the case in steel, the nonideality of the matrix solid solution is expected to be a function of temperature and may enhance the kinetics with decreasing temperature. Also the ledged nature of the interface may be such that the interpretation of the predicted interfacial energy needs to be re-examined.
Another parameter, which is used in the kinetic model, is the matrix diffusivity. The possibility exists that the wrong value of diffusivity is being used in the theory. If disordering takes place in advance of the interface, then the actual diffusivity may be larger than expected from ordered beta phase diffusivity measurements. Figure 5.6 shows a comparison between zinc diffusivity in ordered beta brass and the diffusivity that would rationalize the lengthening kinetics of needles. The diffusivity data is taken from Kuper et al. (69).

The above interpretation of the enhanced kinetics rests highly on conjecture and is not supported by independent experiments. Although there is justification for challenging the interfacial creation and diffusivity assumptions, the evidence is insufficient to conclude that either of these effects is the paramount cause for the failure of the model. There is, however, independent evidence that suggests that the transformation takes place away from equilibrium. This deviation from equilibrium is not explained by either of the two above effects, hence it is wise to investigate the effect of deviation from equilibrium in the application of the model.

In order to establish an equilibrium criteria for the interfacial concentrations it is necessary to refer to the thermodynamics of the coexisting phases. Ordinarily the equilibrium phase diagram provides the needed information to stipulate the proper interfacial concentrations under static conditions for the stable phases. However, it is possible that the kinetic situation is different and metastable equilibrium may be present. Some unknown phenomena may provide the transformation with
Figure 5.6. The temperature dependence of the diffusivity of zinc in beta brass as determined experimentally by Kuper et al. (69) is compared with the predicted diffusivity that would satisfy the needle kinetics.
an added driving force which is responsible for the enhanced kinetics. This type of mechanism has been proposed by Hornbogen and Warlimont (43) to rationalize the enhanced kinetics of alpha plates. In their analysis the diffusion of zinc to stacking faults provides the additional driving force. The identical mechanism, however, cannot operate in the needle situation due to the nonexistence of stacking faults.

It is possible for one to estimate the magnitude of the necessary deviation from equilibrium without understanding its nature. This is feasible due to the character of the free energy versus composition diagram. Figure 5.6 shows such a diagram for the beta and alpha phases, where the free energy due to surface creation has already been taken into account. The solid lines represent the usual free energy functions, whereas the dashed line represents the postulated free energy of the beta phase. The increase in free energy $\Delta G_K$ represents the free energy increase of the beta phase or the free energy decrease of the alpha phase due to the phenomena which is causing the accelerated kinetics. In this instance all the free energy addition is assumed to take place in the beta phase. The free energy addition is taken into account in the same manner theoretically as is done when capillarity is considered. It can be seen from the diagram that the new equilibrium condition given by the dotted tangent line increases the concentration at the interface in both phases such that diffusion is aided and the kinetics are accelerated. The interfacial concentrations are thus a function of the assumed $\Delta G_K$ and can be calculated from thermodynamic data of the two solid solutions for both species, copper and zinc.
Figure 5.7. $\Delta G_K$ increases the equilibrium concentrations at the interface.
These new equilibrium concentrations, $C_P^K$ and $C_Q^K$, are calculated in the same fashion as is done for capillarity, where a curvature dependent equilibrium concentration is calculated from the dependence of chemical potential on curvature. Various values of $\Delta G_K$ can be assumed, and the resultant kinetic predictions can be compared with the data.

It was found that a reasonable fit between the theory and the data could result for a given assumed surface energy for a proper $\Delta G_K$. The additional free energy needed to rationalize the kinetics ranged from 3 cal/mole at 500°C to 117 cal/mole at 250°C for a surface energy of 200 ergs/cm$^2$. For an interfacial energy of 500 ergs/cm$^2$ the corresponding range was 14 cal/mole to 132 cal/mole. Hence, if the assumption is made that some phenomenon or condition is providing the transformation with an added driving force given by the amount $\Delta G_K$, then the kinetics and radii are properly predicted by the theory. However, unless the nature of the source of the $\Delta G_K$ can be understood, this analysis has no physical basis.

Two causes for the apparent $\Delta G_K$ will now be considered. The increase in free energy may be due to the presence of excess vacancies which are quenched in as a result of the homogenization process prior to the isothermal heat treatment used in the measurement of the kinetics. If excess vacancies are present, as most certainly is the case, then the free energy of the beta phase would be increase by an amount $\Delta G_K$. However, a calculation of the magnitude of the free energy of these excess vacancies can only account for a $\Delta G_K$ of 0.2 cal/mole at the most. Hence, this does not appear to be the cause of the apparent $\Delta G_K$. 
A second possible source of additional free energy, $\Delta G_K$, may exist if the matrix is disordered at the interface. The disordered beta phase would have a higher free energy than the ordered phase which would account for a $\Delta G_K$. The order-disorder energy is reported in the literature as about 10 cal/mole (70) and is of the correct order of magnitude. If it could be shown that the ordering energy depends on temperature as was found for $\Delta G_K$, then the present notion would have more credibility. Even if the preceding statement were correct, one cannot rationalize the slightly accelerated kinetics at 500°C on this basis since the order-disordering temperature is about 460°C. Thus, on the basis of the data at 500°C it appears as though the enhancing effect is independent of the ordering reaction. It is therefore possible, but not most likely, that the enhanced lengthening kinetics of alpha needles are due to an order-disordering reaction at the interface. There is no obvious experimental way to ascertain the degree of order at the interface to confirm or discredit the presently stated notion.

Summarizing this portion of the discussion, it has been shown that if an additional free energy is available at the interface, the enhanced kinetics can be predicted by the theory. However, efforts to explain the nature of this apparent free energy, $\Delta G_K$, have failed to produce a satisfactory cause.

Equilibrium considerations at the interface are included in the model for two purposes. The first is to establish a boundary condition for the diffusion equation; the second is to determine the appropriate
solute flux balance at the interface. The second condition dictates
the quantity of solute that must diffuse away from the interface in the
matrix. If a short circuit diffusion mechanism is available, some
solute will diffuse by the short circuit path with the rest diffusing
through the matrix volume. Since the model only applies to the solute
that must diffuse through the volume, the kinetics should be predicted
on the basis of an effective precipitate concentration different from
the equilibrium concentration, providing a short circuit mechanism is
operating. This possible effect is considered in this work in the
following fashion. In the flux balance at the tip interface, the pre­
cipitate concentration is varied to match the kinetics to obtain an
effective precipitate concentration, \( C_p^* \). The difference between the
actual (equilibrium) precipitate concentration, \( C_p \), and the effective
precipitate concentration, \( C_p^* \), represents the solute transported by a
short circuit mechanism. The necessary percent transported by a short
circuit mechanism ranges from 16\% to 40\% for needle lengthening and
an assumed interfacial energy of 200 ergs/cm\(^2\). Thus if a short cir­
cuit mechanism is responsible for the enhanced kinetics, it must
account for as much as 40\% of the total solute transported.

There does not appear to be a short circuit mechanism which could
be responsible for such a large percentage of the solute diffusion.
The interphase interface is often considered to be a possible high
diffusivity path. But under the assumptions of the theory capillarity
always creates an interfacial concentration gradient which opposes,
not aids volume diffusion. There is apparently no experimental
justification for assuming other mechanisms such as dislocation pipe
diffusion or surface diffusion along a free surface. It thus seems
unlikely that any short circuit diffusion mechanism can rationalize
the enhanced lengthening kinetics of alpha needles precipitating from
beta brass.

If the precipitate possesses a composition different from its
expected equilibrium value, then the effect can be included in the model
by assuming a given departure from equilibrium in the precipitate,
$\Delta C_p$. The nonequilibrium precipitate concentration, $C_p$, is varied to
match the kinetics. The kinetic predictions for assumed deviations
from equilibrium are given in Figures 5.9 and 5.10, where the deviation
is given in Table 9 as a function of temperature. There exists x-ray
and electron diffraction evidence that the plate is a metastable struc­
ture which is heavily faulted and possibly even face centered tetragonal.
In this case the metastable alpha prime would have a different free
energy dependence from alpha, which produces a higher precipitate con­
centration under this metastable condition. Figure 5.8 shows the con­
dition where the metastable precipitate concentration is given by $C_p$.
It is assumed that the difference in free energy between the stable
and metastable phase is small, therefore $C_o$ is essentially the same in
both instances. Qualitatively the relationship between the free energy
functions for alpha and alpha prime shown in Figure 5.8 is not unreas­
sonable. It would be expected that the difference between the two
would be least for high zinc content, since zinc lowers the stacking
fault energy. It is not so clear why this behavior would be manifested
Figure 5.8. The metastable precipitate $\alpha'$ is shown in this schematic diagram to increase the precipitate concentration by $\Delta C_p$.
Figure 5.9. Needle kinetics for nonequilibrium and $\sigma = 200$ ergs/cm$^2$. 

VELOCITY, CM/SEC. vs. $(C_0 - C_\infty)$ MOLE FRAC. ZINC

500°C, 450°C, 400°C, 350°C, 300°C, 250°C
Figure 5.10. Plate kinetics for nonequilibrium and $\sigma = 200$ ergs/cm$^2$. 
Table 9. The magnitude of the predicted deviation from equilibrium in the precipitate is shown as a function of temperature

<table>
<thead>
<tr>
<th>Temperature °C</th>
<th>Needle ΔC_p at. % Zn</th>
<th>Plate ΔC_p at. % Zn</th>
</tr>
</thead>
<tbody>
<tr>
<td>250</td>
<td>4.5</td>
<td>5.0</td>
</tr>
<tr>
<td>300</td>
<td>1.6</td>
<td>3.0</td>
</tr>
<tr>
<td>350</td>
<td>2.2</td>
<td>1.5</td>
</tr>
<tr>
<td>400</td>
<td>1.5</td>
<td>---</td>
</tr>
<tr>
<td>450</td>
<td>1.8</td>
<td>---</td>
</tr>
<tr>
<td>500</td>
<td>1.0</td>
<td>---</td>
</tr>
</tbody>
</table>
in the case of the nonfaulted needles, unless faults are present at the growth front but anneal out behind the interface. Flewitt and Towner (67) have measured precipitate concentrations as a function of isothermal annealing time for plates at 250°C and needles at 500°C. Their results are shown in Figure 5.11 along with the presently predicted concentrations. It is seen that during the annealing times in which the growth data was taken, the agreement is excellent. The alpha concentration is greater than the equilibrium concentration as predicted by the present analysis. This lends strong support for the situation described in Figure 5.8. It is observed in Figure 5.11 that for sufficiently long annealing times the metastable precipitates transform into the lower concentration stable phase.

If the internal structure is influencing the kinetics, then the needle to plate transition may result from the differences in internal structure of the plate and needle. Hence, it appears to be possible to rationalize the kinetics, radii, and morphological transitions if the plate and needle are metastable phases.

The tip radii are also predicted by the theory, for an assumed interfacial energy and deviation from equilibrium. Purdy has measured the tip radii of alpha needles at 400°C. His results are shown in Table 10 together with the theoretical predictions for interfacial energies of 200 and 500 ergs/cm². It is observed, for the semicoherent interfacial assumption, that the results are in agreement for both interfacial equilibrium and a deviation from equilibrium. The agreement is better, however, for the assumed deviation from equilibrium.
Figure 5.11. The precipitate concentrations predicted by the present analysis are compared with the experimental measurements of Fiewitt and Towner (67).
Table 10. The experimental and predicted radii of curvature are compared for needle growth at 400°C. The agreement is seen to be best for the assumption of nonequilibrium and an interfacial energy of 200 ergs/cm²

<table>
<thead>
<tr>
<th>Alloy Composition at. % Zn</th>
<th>Tip Radius of Curvature, Å</th>
<th>σ = 500 ergs/cm²</th>
<th>σ = 200 ergs/cm²</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Equilibrium</td>
<td>Nonequilibrium</td>
<td>Equilibrium</td>
</tr>
<tr>
<td>41.1</td>
<td>1170</td>
<td>595</td>
<td>430</td>
</tr>
<tr>
<td>44.1</td>
<td>6488</td>
<td>5534</td>
<td>2595</td>
</tr>
</tbody>
</table>
An interfacial energy of 500 ergs/cm² predicts radii which are far outside the range of the measured values. These observations support the conclusion made from the kinetic analysis that the interface is semi-coherent, and that both the kinetics and radii are properly rationalized if deviation from equilibrium is assumed. In addition, the predicted deviation from equilibrium in the precipitate is observed from independent microprobe experiments.

The partitioning of the supersaturation was calculated from Equations 3.3 and 3.8, and the results are shown in Figure 5.12 for a needle and plate at 300°C for the concluded deviation from equilibrium. Capillarity is seen to play a lesser role as the driving force $C_o - C_\infty$ is increased. This result is similar to that found for the growth of Widmanstätten ferrite, as is expected.

In summary, measured edgewise growth kinetics of alpha precipitating from beta brass are shown to be faster than predicted for the assumption of interfacial equilibrium. Although effects associated with interfacial creation and the assumed diffusivity could enhance the kinetics, it is concluded from precipitate concentration data that the enhanced kinetics were primarily due to deviation from equilibrium in the precipitate. Excellent agreement exists between the model and the kinetics and radii for an assumed interfacial energy of 200 ergs/cm² and an assumed deviation from equilibrium. These conclusions are in agreement with those drawn from the precipitation kinetic studies of Widmanstätten ferrite growth from austenite. The volume diffusion model is good if the tip interface is semicoherent and if departure
Figure 5.12. Normalized supersaturation is divided between diffusion and capillarity at 300°C for (a) the needle and (b) the plate.
from equilibrium is considered and is consistent with independent experiments.

Lengthening Kinetics of Beta Sideplates in Alpha Brass

The reverse transformation of precipitating the beta phase from the alpha phase is of interest for several reasons. Primarily it permits the study of two transformations which have the same interface but differ with respect to the nature of the precipitate and matrix phases. The plate shape and slow growth are exhibited by both alpha and beta precipitates, although the beta precipitates do not exhibit a surface relief. There is no basis for postulating that this transformation takes place by a shear mechanism both because of the lack of observed surface relief and the low supersaturation. Thus if both transformations exhibit the same growth characteristics, then this would support the notion that a real shear may not exist for the beta to alpha transitions.

For an assumed interfacial energy of 200 ergs/cm$^2$ the theory of Trivedi predicts that the lengthening rate at 665°C in a 37.6 at % Zn alloy should be $5 \times 10^{-6}$ cm/sec. This is to be compared with the measured kinetics of $7.5 \times 10^{-5}$ cm/sec. The theory predicts a radius of curvature at the tip of 4000 Å. These calculations were made on the basis of nonideality of the two phases. Although the measured kinetics are fifteen times faster than predicted, the large uncertainty in the diffusion constant for alpha brass, makes any definite conclusion unreliable. The diffusivity of copper and zinc is known to be a strong
function of concentration in the present range of interest (71). The diffusion constant has to be extrapolated nearly 10 at % from the measured value at 28 at %. The lengthening kinetics do appear to be enhanced, however, no great weight can be given to this observation until the copper and zinc diffusivities in the alpha phase are determined to a greater accuracy in this concentration range of interest.
CHAPTER VI: WIDMANSTÄTTE GROWTH IN OTHER SYSTEMS

Introduction

The Interpretations of the iron-carbon and copper-zinc kinetic and radii data are specific and apply to each system individually. There is an inherent danger in analyzing a narrow set of data with a flexible multiparameter model. This information by itself has limited value, as conclusions may only apply to those specific systems. The underlying reason for studying these transformations is to develop general criteria for the mechanism and growth characteristics of plate-like and needle-like diffusional precipitation in the solid state. To add validity to the interpretations, it is necessary to examine the widest possible gamut of data available on the phenomena. The main difficulty with examining transformations in other systems is that the diffusion and thermodynamic data are usually not as dependable as in steel and brass. In addition, other dubious nuances may complicate the analysis. Nonetheless, it is still beneficial to examine kinetics in other systems to at least gain a qualitative understanding of these transformations. The objective of the present chapter is to investigate other systems to see if they are consistent with the conclusions drawn from the analyses of iron-carbon ferrite and copper-zinc alpha. The basic conclusions are that the precipitate edgewise growth rate is dictated by volume diffusion, deviation from equilibrium, and the coherency of the interface.
The following transformations will be considered: the growth of upper bainite, lower bainite, cementite plates, Mo\(_2\)C needles, and grain boundary ferrite in steels; Widmanstätten austenite from iron-nitrogen ferrite; theta prime plates from Al-4% Cu; and alpha plates from beta titanium-chromium. This collection of precipitation processes involves a wide variety of individual characteristics, although all but the grain boundary ferrite exhibit a plate or needle morphology and diffusional growth. Thus, if volume diffusion and interfacial structure are the dominant characteristics of the transformation, then the theoretical analysis should bear this out. If the analysis does not bear this out, the discrepancy may indicate what assumptions of the theoretical model are not justifiable.

Ferritic Transformations in Steel

It has been suggested by previous workers, notably Hillert (40), and Kaufman, Radcliffe, and Cohen (46) that the transformations, Widmanstätten ferrite, upper bainite, and lower bainite are continuous with respect to kinetics and transformation mechanism, suggesting that the plate morphology and volume diffusion determine the growth kinetics. The carbide precipitation is different in the three cases but is purported to play a minor role in determining the edgewise growth rates. It is of interest in the present work to see if the plate growth model can be extrapolated continuously through the three transformation regions.

The analysis of the Widmanstätten ferritic kinetic data implies that an undetermined interfacial process is apparently retarding the
kinetics, although it could not be ascertained what this process is. Two interpretations are offered to explain the retardation. The first is that the mobility of the iron is slow enough to necessitate a finite driving force to transport it across the interface. The second theory is that a certain quantity of driving force is consumed at the interface, but the amount consumed is independent of the rate of motion of the interface. The driving force may not in actuality be consumed at the interface but it is in the value of the interfacial concentration that the effect is manifested.

Since it has been discovered that alloying can affect the self-diffusion of iron in austenite, it is reasonable to expect a similar effect in the austenite-ferrite grain boundary. The effect of carbon on the mobility of iron in austenite has been discussed in Chapter IV. Nickel \(^{(72)}\) and chromium \(^{(73)}\) also influence the self-diffusion of iron in austenite, so alloys containing these elements were analyzed with respect to the present model.

Speich and Cohen \(^{(15)}\) have measured the growth rate of bainite in pure iron-carbon and also in Fe-Ni-C and Fe-Cr-C alloy systems. It is of interest to analyze the role of nickel and chromium as they effect the interfacial mobility. Nickel is an austenite stabilizer and chromium is a ferrite stabilizer, hence it would be expected from an overall driving force point of view that the two would have opposite effects on the kinetics. However, the empirical results indicate that the addition of 2.7% Cr has the same effect as the addition of 5.2% Ni. Both additions retard the kinetics by an order of magnitude.
Gruzin and Kuzetsov (72) have studied the effect of carbon and nickel on the self-diffusion of iron in austenite in Fe-Ni-C alloys. If the activation energy for boundary diffusion is one half of that for bulk diffusion, the addition of 20% Ni to Fe-15 at% C increases the estimated boundary diffusion of iron by a factor of 1.2. Hence, the addition of Ni has a very weak effect on mobility for a given carbon concentration. These results indicate that the effect of Ni does not directly rationalize the order of magnitude retardation in the kinetics. Rao et al. (74) have shown that the addition of nickel has a major effect on the \(\alpha+\gamma\), \(\gamma\) phase boundary in that it can shift the boundary down by several atom percent carbon. Consequently, the equilibrium carbon concentration at the interface is lowered drastically. If one takes the reduction of 6 at % C into account in calculating the boundary self-diffusion of iron with the addition of 5 wt % Ni, one finds that the boundary diffusion coefficient is reduced by a factor of six. The assumed reduction of 6 at % C corresponds to the phase boundary change due to the addition of 5 wt % Ni. Similarly the addition of 10 wt % Ni reduces the mobility by a factor of 16. The reduced carbon concentration, therefore, could reduce the mobility by an order of magnitude. Thus, it is possible that the nickel retards the motion of the interface indirectly as it changes the interface concentration.

The retardation due to chromium appears to result directly from the effects of chromium itself, not indirectly through its influence on the interfacial carbon concentration. If one considers
pure iron-chromium, then the addition of 2.7 wt % Cr reduces the expected boundary self-diffusion of iron by a factor of ten. No data exists for the effects of chromium on Fe-Cr-C alloys or the expected position of the $\alpha + \gamma, \gamma$ phase boundary as a function of chromium content at hypoeutectoid temperatures. However, from the limited data available (73) it seems most likely that the addition of chromium retards the bainitic reaction because of the direct influence chromium has on the self-diffusion of iron, and hence, the interface mobility.

Through this analysis it has been assumed that the boundary pre-exponential diffusion coefficient is proportional to the austenitic pre-exponential coefficient. The only ferrous data available is for the addition of manganese to iron (75). The assumed parallel dependence is seen in Figure 6.1, with the results agreeing best for compositions below 4 wt % Mn. In addition to this data, it is observed that grain boundary pre-exponential diffusion coefficients in metal systems are generally of the same magnitude as the corresponding coefficient for bulk diffusion. Therefore, it appears to be reasonable to assume that the grain boundary pre-exponential coefficient is proportional to that for bulk diffusion.

Although the above discussion indicates that the qualitative bainitic growth rate may be rationalized by the effect of alloying elements on interfacial mobility, it is necessary to look further into the dependence of edgewise growth velocity on driving force to get a more detailed understanding. Rao and Winchell (13) have measured the lengthening rates of upper bainitic plates over a wide range of
Figure 6.1. The effect of Mn on the pre-exponential diffusion coefficient of iron in the boundary and the volume are compared.
supersaturation. The temperature of the measurement was 400°C, only
50°C below the lowest temperature of the Widmanstätten ferritic trans-
formation studied in this work. Thus, if there is some continuity
between the Widmanstätten ferritic transformation and upper bainite,
then the same kinetic rationalization should apply to both types of
precipitates.

Figure 6.2 shows three theoretical predictions based on three
different kinetic assumptions. The curve for an infinitely mobile
interface clearly shows that the wrong order of magnitude of growth
kinetics is predicted. Thus, it is concluded that in the case of
upper bainite the interface is being retarded. The case for finite
interfacial mobility is predicted from the mobility expected from the
Widmanstätten ferritic data. It is seen that the correct order of
magnitude is predicted, although the dependence on supersaturation is
not as measured experimentally. The case where an amount of super-
saturation, $\Delta C_K$, is consumed at the interface but is independent of
velocity, is shown to fit the data best. This implies that Hillert's
interpretation of the interfacial resistance is more appropriate.
Thus if upper bainite and Widmanstätten ferrite grow by the same
mechanism, then it is more reasonable to interpret the Widmanstätten
kinetic data according to Hillert's notion.

It is not possible to measure the interfacial concentration
directly, although Houillier, Bégin, and Dubé (76) have developed an
indirect technique to estimate the deviation from equilibrium for
the growth of upper and lower bainite in a manganese steel. By
Figure 6.2. The edgewise growth rates for upper bainite are compared with the model for three different interfacial assumptions.
measuring the austenitic composition as a function of reaction time, they were able to estimate the austenite-bainite interfacial concentration. This should correspond to the interfacial concentration of austenite in metastable equilibrium with ferrite. Such measurements confirm that the interfacial concentration is inconsistent with the extrapolated phase boundary, as is predicted from the present kinetic analysis for the growth of upper bainite in an Fe-Ni-C alloy.

Kinsman and Aaronson (77) have observed the motion of a flat ferrite-austenite interface in Fe-C, Fe-Mn-C, and Fe-Mo-C alloys. In all systems parabolic diffusional growth is observed, although only the addition of molybdenum retards the interfacial motion. It is concluded by Kinsman and Aaronson that the molybdenum produces a drag effect on the interface, which retards the diffusional growth. The drag effect observed in the Fe-Mo-C system may be related to the interfacial resistance observed in Widmanstätten ferrite and upper bainite.

There are two important differences between the lengthwise growth of Widmanstätten ferrite and the thickening of grain boundary ferrite. First, the thickening rate is one to two orders of magnitude slower than the lengthening rate, therefore the rate of atomic transfer across the interface is of much less importance when considering the thickening kinetics of the grain boundary precipitates. Secondly, the Widmanstätten platelet radius influences the kinetics, whereas the grain boundary ferrite has no curvature. The kinetics of lengthening are determined by both the diffusional driving force and the
mobility dependent radius, but the thickening can only be retarded by reducing the driving force for diffusion. For these two reasons alone, it is safe to conclude that the short range diffusion of atoms across the interface should not strongly influence the thickening rate of grain boundary ferrite. In addition, Kinsman and Aaronson have shown that a good parabolic fit can be made with the thickness versus time data over a range of times which have velocities varying by over an order of magnitude. This indicates that the retardation of the interface is not dependent on how fast the interface moves. The implication is that atomic transfer across the interface cannot be responsible for the observed retarded kinetics. As was done for the case of Widmanstätten ferritic and upper bainitic lengthening, a shift in the $\alpha+\gamma,\gamma$ phase boundary was made in order to predict the measured kinetics. The shift in the phase diagram was then used to calculate the amount of energy which is being consumed by the transformation other than for volume diffusion of carbon and interfacial creation. This energy is plotted in Figure 6.3 as a function of temperature.

It is instructive to compare the magnitudes of the processes consuming energy for the various ferritic processes in the graph shown in Figure 6.3. Such a comparison shows that the energy consumed by the Widmanstätten transformation is consistent with that predicted for upper and lower bainite. Thus, if one utilizes Hillert's interpretation for all three transformations, then it could be concluded that the lengthening rates of the precipitates are influenced by the same processes. This total analysis gives strong support to the
Figure 6.3. The energy consumed by an interfacial thermodynamic effect for three different transformations as a function of temperature.
interpretation of Hillert. Although the magnitude of the predicted grain boundary mobility was reasonable, the evidence from other ferritic transformations strongly suggests that interfacial mobility is not responsible for the retarded kinetics. The interfacial mobility interpretation of the Widmanstätten ferritic kinetic data can be considered valid only if the transformation mechanism for Widmanstätten ferrite is different from that for upper bainite.

Figure 6.4 indicates the energy consumed by the Widmanstätten ferritic interface as a function of temperature. In addition, the consumption of the diffusional and capillarity processes are included to illustrate the relative strength of the effects. In the case of both Widmanstätten ferrite and grain boundary ferrite (Fe-Mo-C), Figures 6.3 and 6.4 indicate that there is no necessity for any deviation from equilibrium at temperatures above the eutectoid temperature. The free energies are calculated on the basis of pure iron-carbon thermodynamic data. The influence of alloying elements on the free energy differences of austenite is not included in Figure 6.3.

Now that it has been established that there exists a process which consumes energy for the various ferritic transformations, it is germane to ask what this process might be. A very likely explanation is that strain accompanies the transformation and this might be responsible. This purports that a certain fraction of the supersaturation must be relieved to compensate for the building up of strain energy. This fraction of the supersaturation is not available to drive the volume diffusional process. The difficulty with accounting
Figure 6.4. Free energy which volume diffusion, the interface kinetics, and capillarity consume for the 0.24% C alloy as a function of temperature.
for the strain is a serious problem, which arises from many complications. These complications result from the elastic and plastic nature of the strains, the detailed role of dislocations, the effective range of the precipitation stresses, the difference in mechanical properties of the precipitate and matrix, and the influence of precipitate morphology. Certainly strain must enter the picture somehow, but it eludes us to discover just how. One might rationalize that the strain is relieved by interfacial dislocations in such an array and orientation that the long range strains do not develop, because the strains are canceled on a short range basis. Although this might be a true explanation, it is not very satisfying. The fact that a substantial $\Delta G_K$ is also observed for grain boundary ferrite with an entirely different shape also indicates that perhaps bulk strain is not responsible for the retarded kinetics.

Equilibrium concentrations as determined from phase diagrams apply to equilibrium at interfaces which are disordered. The coherency manifested by the Widmanstätten transformation may alter the expected local equilibrium criteria. Larché (78) has investigated the possible effect of coherency on equilibrium and has shown that coherency affects equilibrium in the same direction as predicted in this research. However, the treatment is highly theoretical and not easily manageable to make the appropriate calculations for the present case. It does seem worthwhile to use this treatment to estimate quantitatively the effect of coherency on equilibrium. The coherency argument would apply to the growth of grain boundary ferrite if it
also were coherent.

If the interface is coherent and can only advance by the nucleation and growth of ledges, it might be necessary to have an undercooling present at the interface to establish a reasonable rapid rate of ledge nucleation. If the undercooling were not present, the ledge nucleation rate may be almost nonexistent and thus act as a growth barrier.

Another alternative explanation for the retarded kinetics is the possibility of carbide precipitation or nucleation which may be consuming the free energy that is manifested in the retarded kinetics. It must be realized that the region in advance of the precipitate has a concentration which is in the region of metastable coexistence of cementite and austenite. Thus, it is possible that preliminary stages of precipitation of cementite may be taking place in front of the interface. Although actual cementite is not observed, there may exist clusters which relieve a portion of the supersaturation. It is difficult to describe in detail what this process is except to say that there can exist some competition for the available driving force between the ferrite and the carbide. The excess driving force $\Delta G^*_K$ is noted to vanish as the eutectoid temperature is approached for both Fe-C Widmanstätten ferrite and Fe-Mo-C grain boundary ferrite. In addition, it will be noted later in this chapter that the hypoeutectoid beta to alpha transformation in titanium-chromium also is retarded.

In summary, Widmanstätten ferrite in pure iron-carbon, upper bainite in iron-nickel-carbon, and grain boundary ferrite in a
molybdenum steel all manifest reaction kinetics which are slower than expected from local equilibrium and volume diffusional considerations. Although the interfacial mobility concept can account for the retarded kinetics of Widmanstätten ferrite, it fails to rationalize the kinetics for the reaction of upper bainite in a nickel steel. Strain and coherency arguments may account for the kinetic discrepancy for the platelet precipitates but are inconsistent with the grain boundary ferrite precipitation. The possibility that carbide precipitation may be competing for the available free energy is real and could account for the manifested reaction kinetics of all four transformations. The most realistic conclusion, physically, is that the kinetics of these transformations are being retarded by a thermodynamic effect, which is consistent with the notion of Hillert but inconsistent with the concept of interfacial mobility. Principally, however, the edgewise growth rates of Widmanstätten ferrite and bainite are concluded to be dictated by volume diffusion of carbon and the semicoherent structure of the precipitate-matrix interface.

Edgewise Growth of Cementite Plates

Heckel and Paxton (16) have measured the lengthening kinetics of Widmanstätten cementite plates in steel. They analyzed the data on the basis of the Zener-Hillert equation and concluded that the presence of silicon in the alloys resulted in a retardation of the transformation. If the data is re-examined in light of the present model, it is discovered that the experimental results are much more rapid than expected from theory (79). Thus, it appears that the
discrepancy is in the opposite sense as purported by Heckel and Paxton. Other relevant data on the reaction kinetics of cementite has been reported by Nolfi, Shewmon, and Foster (80). They observed the precipitation of spherical cementite from ferrite and concluded that the interface is strongly immobile and the reaction rate is reduced by order of magnitude. It is not expected that there should be such a gross disparity between the reaction characteristics of the two cementite transformations. The kinetic discrepancy for cementite plate growth is believed to be due to a weakness in the model of Trivedi, which arises under conditions of small transformation driving forces. It is possible that anisotropy in the interfacial mobility may be responsible for the enhanced experimental kinetics.

Edgewise Growth of Austenite in Iron-Nitrogen

A transformation closely related to steel is the precipitation of austenite from ferrite in the iron-nitrogen system. The edgewise growth kinetics of these precipitates have been determined and reported by Grozier (18). The experimental arrangement for observation of this reaction is unique in that the supersaturation is established by altering the alloy composition instead of the temperature. One serious defect in this technique is that the original matrix is not homogeneous with respect to composition. Nitrogen is introduced at the free surface and allowed to diffuse into the bulk, hence the concentration is greater at the surface than at an interior location. As more nitrogen is dissolved into the ferrite, the ferrite becomes
supersaturated and austenite eventually precipitates at the surface with either a platelet or needle shape. The precipitate lengthens with time, and the lengthening is believed to be controlled by local equilibrium between the austenite, ferrite, and the gas phase and by volume diffusion of nitrogen in the solid.

Grozier analyzed the lengthening kinetics with the Zener-Hillert model and concluded that the model properly rationalized the kinetics and that there existed no interfacial process which retarded the kinetics. The actual morphology of these precipitates is most certainly closer to a needle than a plate due to the decreasing supersaturation with depth into the sample. Growth normal to the free surface should be prohibited because of the lack of driving force in this direction. Thus, the present model for needle growth was compared to the data, and the results are shown in Figure 6.5 for an assumed semicoherent interfacial structure. It is seen that the predictions underestimate the observed kinetics. As in the precipitation of cementite, the precipitation takes place with very little supersaturation in the matrix, and it is believed that the model needs to be revised to match the kinetics.

**Edgewise Growth of Theta Prime in Al-4% Cu**

Aging of Al-4% Cu also produces a Widmanstätten structure consisting of theta prime plates imbedded in an alpha matrix. This process plays an important role in age hardening of aluminum alloys, thus there is technological interest in this alloy in addition to scientific interest. Laird and Aaronson (81) have performed elaborate experiments
Figure 6.5. The edgewise growth rate of austenite in Fe-N is shown as a function of driving force.
to observe the structure of these precipitates and to determine the edgewise growth rates. Transmission electron micrographs have revealed the dislocation structure of the sides of the plates. The mismatch between the precipitate and matrix is accommodated by an array of dislocations arranged to produce a hexagonal configuration. The atomistic structure of the sides is believed to consist of a series of ledges such that sidewise growth can only be accomplished by the lateral motion of the ledges. The lengthening kinetics and tip radii were determined and compared with several diffusional models, and it was concluded that all the models predicted rates much slower than those measured. The present model was compared with the kinetic and tip radii data. The conclusion is drawn that the predicted velocities are about one order of magnitude too small and that the predicted radii are also about one order of magnitude too small. This presents the third transformation, in addition to cementite and iron-nitrogen austenite, in which the predicted kinetics are much slower than the measured kinetics for a low matrix supersaturation. It appears that certain assumptions of the model relating to the precipitate shape or interfacial mobility are not valid for low driving forces.

Edgewise Growth of Mo$_2$C Needles from Ferrite

An exception to the above kinetic conclusion for low supersaturations is the precipitation of Mo$_2$C needles from ferrite in a molybdenum steel. Hall, Kinsman, and Aaronson (27) have recently studied this transformation and have measured the tip radii and lengthening rate from transmission electron micrographs. They analyzed the data.
utilizing the Zener-Hillert model and found good agreement between the predicted and measured kinetics. The present rigorous needle model was used in this work, and it too is found to be in agreement with the kinetic measurements. In addition, the experimental radii were predicted for an assumed interfacial energy of 540 ergs/cm² and ideal solution behavior. Hence, this transformation is rationalized for an assumed disordered interface and is in conflict with the other kinetic data in two respects. First, the matrix supersaturation is small, but the measured kinetics are predicted even though this is not the case in all the other systems. Second, the systems which are known best, pure iron-carbon and copper-zinc, manifest a coherent interface, whereas the Mo₂C data predict an incoherent interface. The molybdenum carbide data does not fit the general conclusions of this thesis, and it is not apparent why this inconsistency exists.

Edgewise Growth of Alpha from Beta Titanium-Chromium

The last transformation considered in this thesis is the precipitation of alpha plates from beta titanium-chromium. The experimental edgewise growth rates have been reported by Aaronson (34), who analyzed the data with the use of the Zener-Hillert model. The data has been presently analyzed in light of the rigorous model and an assumed semicoherent interfacial energy. It is concluded that the measured kinetics are retarded by about an order of magnitude with respect to the predicted results for large supersaturations, where \( \Omega_0 \) is greater than 0.3. However, the single data point for a small supersaturation is about one order of magnitude faster than predicted.
These results are consistent with the kinetic trend observed in this thesis. The model typically underestimates the kinetics for small supersaturations.

The necessary diffusion and thermodynamic data in titanium-chromium is not reliable enough to make a quantitative analysis, as was done for the case of Widmanstätten ferrite; although the transformation does exhibit some important similarities to the iron-carbon transformation. In particular, the phase diagram in the region of interest possesses a eutectoid reaction, which may retard the kinetics in the same manner as was suggested for the precipitation of ferrite from austenite. The precipitation or nucleation of TiCr₂ may consume free energy, as was proposed for the influence of Fe₃C during the ferritic transformations.
CHAPTER VII: DISCUSSION AND CONCLUSIONS

Interfacial Structure

Although several systems have been analyzed qualitatively, only the edgewise growth of Widmanstätten ferrite in steel and Widmanstätten alpha in brass have been interpreted quantitatively. The quantitative study reveals that the tip interface possesses a large degree of coherency. This suggests that the atomistic nature of the plate edge is stepped and that growth normal to the broad faces of the steps is accomplished by lateral motion of the ledges. It is germane to explore the effects of the ledge structure on the assumptions of the theory, which are related to the nature of the interfacial boundary.

Before undertaking an elaborate discussion of the ledges themselves, it is pertinent to investigate the possibility that the low interfacial energy may be a result from a shear transformation mechanism. The interfacial energy of 200 ergs/cm$^2$ is also what is believed to be the energy of a martensitic interface. If the shear argument is correct, then the interface must advance at a discontinuous rate in such a fashion that a volume element of austenite is transformed into ferrite of the same composition. The solute partitioning takes place before and/or after the element is sheared but not simultaneously as the interface advances. Aaronson (12) has developed thermodynamic arguments which place restrictions on the feasibility of such a transformation. It is stated that if the partitioning takes place prior to the shear, then the solute has to diffuse uphill to reduce the volume
element concentration as shown in Figure 7.1.b. $C_i$ is the concentration near the interface predicted from the volume diffusion model.

If the partitioning takes place after the shear, it is seen from Figure 7.1.c that such a process is accompanied by an increase in free energy if the concentration, $C_i$, of the volume element is greater than $C^*$, defined in Figure 7.1.a. Hence, this reaction sequence cannot take place spontaneously. Thermodynamics will not allow partitioning either before or after the volume element shears. It can be concluded that the shear and partitioning cannot coexist as transformation characteristics provided that the interfacial concentration is greater than $C^*$. In both the cases of alpha-beta brass and steel, the interfacial concentrations are predicted to be greater than $C^*$. Thus, the volume diffusion analysis and the manifested interfacial energy together presage that the transformation proceeds by ledge motion and not by a cooperative shear.

The details of the interface were not specified in the development of the kinetic model. The major assumptions concerning the interface itself were its macroscopic parabolic shape, its curvature which implied that interfacial creation must accompany growth, and its role as a boundary separating the austenite from the ferrite such that its motion is manifested by the transfer of mass from the matrix to the precipitate. These three characteristics will now be examined to render a more realistic physical description of the interfacial transformation processes.
Figure 7.1. (a) If the volume element at the interface transforms by a shear with no composition change, it must have a concentration less than $C^*$ to transform spontaneously. $C^*$ is that composition where $G^\alpha = G^\beta$. (b) Partitioning prior to the shear necessitates uphill diffusion. (c) Partitioning after the shear is not spontaneous, since the composition $C_i$ is greater than $C^*$.
The morphological assumption of parabolic symmetry has both experimental and theoretical justification. Experimentally, the tip of the precipitate closely resembles a parabola. The assumption of exact parabolic shape is a theoretical convenience, which facilitates solving the diffusion equation. The solution to the diffusion equation in parabolic coordinates should approximate the more realistic solution for a stepped geometry, provided the step dimensions are small in comparison to the macroscopic shape of the precipitate. This condition is satisfied for Widmanstätten ferritic plates and alpha needles in brass, as has been revealed by electron micrographs. Hence, from a standpoint of volume diffusion the model is consistent with the predicted ledge character of the interface.

Interface is created or destroyed when a curved boundary moves normal to itself. The introduction of the effect into the model was made under the assumption that the interface was continuously curved, hence the local curvature was calculated from the assumed parabolic shape. The conclusions drawn from the data hint that the interface is stepped, thus it may not be proper to calculate the local rate of interfacial creation from the shape of a parabola. A uniform density of steps having the same height and orientation will produce a flat macroscopic surface. However, when gradients in step density are present, the macroscopic shape will be curved as seen in Figure 7.2. Blakely (82) has discussed this situation in comparing gradients in step density to gradients in macroscopic curvature. Macroscopically, a curved interface will flatten to reduce the interfacial area and, hence, the
Figure 7.2. The drawings indicate that (a) equally spaced ledges result in a flat macroscopic interface, although (b) unequally spaced ledges result in a curved macroscopic interface.
total energy. Atomistically, a curved interface flattens to produce a uniform distribution of ledges under the driving force of strain. Hence, in both situations the curved interface will flatten, and a correspondence can be drawn between the apparent macroscopic interfacial energy manifested by curvature gradients and the elastic interaction of neighboring ledges existing in a ledge density gradient. Using Blakely's treatment, the apparent interfacial energy can be correlated to the pairwise interaction energy of neighboring ledges. This correlation shows that an interfacial energy of 200 ergs/cm$^2$ corresponds to a pairwise interaction of 0.269 dyne/cm for an interaction distance of 100 Å. This is about two orders of magnitude smaller than the pairwise interaction of parallel dislocations. In the present case of ledges present at a sharply curved interface, the ledge density is too high to expect Blakely's analysis to be reasonable. However, heuristically the treatment is important in that it renders a quantitative and descriptive feeling for the effect of ledge-ledge interactions on the growth of a curved interface.

The instantaneous local rate of interfacial creation has to be reconsidered in light of the predicted stepped interface. Tiller and Jindal (83) have reviewed the problem of growth of a stepped interface and have shown how the interfacial creation must be taken into account. New interface is created only locally at ledge nucleation sites provided ledges are never annihilated, although if ledges are annihilated, then both nucleation and annihilation must be considered. The lateral motion of ledges alone does not change the
net interfacial area since there is simultaneous interfacial annihilation at the bottom of the ledge and interfacial creation at the top.

The broad faces of Widmanstätten plates possess a large degree of coherency, hence it is expected that the ledges at the tip also would exhibit broad faces parallel to the sides of the plates. Although this is most likely, ledges only in this orientation cannot generate the sharply curved tip and still maintain a large degree of coherency. Possible orientations for the ledges are shown in Figure 7.3. The steps are parallel to the sides at position A, parallel to the tip at position C, and at an intermediate orientation at position B.

It is assumed in the drawing that the actual precipitate tip consists of a number of facets, which result from the nucleation and growth of ledges on the interface. The normal growth of this interface results in a net interfacial creation, which can be seen from the following discussion. Consider a polygon which is faceted and contains n equilateral sides meeting at an angle 2\(\theta\). 2\(\theta\) is given by \(90^\circ - \frac{180^\circ}{n}\). It is easily shown from geometry that the rate of area creation with respect to volume creation is proportional to that for a circular cylinder. The proportionality constant is \(\frac{1}{\cos^2 \theta}\) and is unity in the limit of a polygon possessing an infinite number of sides. The error in estimating the interfacial energy for an octagonal cylinder is less than 10% if a circular cylindrical shape is assumed.

Hence, the total interfacial creation accompanying the transformation is not greatly influenced by the atomistic shape of the
Figure 7.3. Possible orientations of ledges on the Widmanstätten plate tip. The lower drawing illustrates the net creation of terrace interface.
interface. However, the local interfacial creation is strongly affected by the details of the interface. It is observed in Figure 7.3 that the faceted interface advances by ledge interfacial creation at ledge nucleation sites and terrace creation at ledge annihilation sites. The ledge creation and annihilation cancel, although there is a net increase in terrace area. This is in agreement with the prediction of the diffusional growth concerning interfacial creation.

The model predicts a low energy interface, which the terrace is expected to possess. The local situation is different for the stepped and continuous interfacial shapes. The model assumes that each position along the interface has to contribute energy for interfacial creation and that the contribution is directly related to the local curvature. In the faceted description, however, each position does not contribute. In fact some positions, where ledges are annihilated, actually receive an energy contribution. Only ledge nucleation sites contribute to this process, thus the local interfacial creation will be determined by the distribution of ledge nucleation sites.

In effect, the assumption of a continuous interface corresponds to an assumed distribution of nucleation sites which is proportional to interfacial curvature. This correspondence may not be too unreasonable, if it is remembered that the tip is where the normal growth velocity and the curvature are the greatest. The larger the normal velocity, the greater is the number of steps that will have to be nucleated to support that growth. It is expected that a large curvature would require a greater number of steps at different orientations;
hence, in this case also, the nucleation of steps should be higher at the tip. Thus, the assumed dependence of local interfacial creation on interfacial position may not be as serious an error as might be thought.

The theoretical model has predicted that a significant deviation from equilibrium can exist at the interface during Widmanstätten transformations. Such deviations can be rationalized in terms of the stepped interface without altering the conclusions drawn from the continuous interfacial assumption. In addition, some new considerations might be introduced such as the energy of interaction between ledges and nucleation characteristics of the ledges.

In summary, the structure of the interface even at the sharply curved tip has been concluded to be stepped and principally coherent. Growth normal to the precipitate interface is accomplished by nucleation and lateral motion of the steps. The diffusional aspects of the model are not affected by the discrete ledge structure, although the notion of interfacial creation needed to be reinterpreted. Local interfacial creation is only found at step nucleation and annihilation sites, but the net interfacial creation results in an increase of only semicoherent interface at sites of ledge annihilation. The net increase of semicoherent interface is manifested by the prediction of the model that the interfacial energy is 200 ergs/cm². The apparent deviation from equilibrium can be interpreted in the same manner for stepped growth as for continuous growth in addition to considerations of interactions and nucleation of steps.
The Model for Small Supersaturations

As mentioned earlier, theory (10) and experiment are in reasonable agreement for large driving forces but are in disagreement for small driving forces with the exception of Mo$_2$C precipitation. Provided the driving force is large, the model gives an adequate description of the transformation process. The model, however, is deficient at low supersaturations, and this matter will not be discussed.

An important aspect of the theory for large driving forces is that the effective distance of diffusion is short, whereas for small driving forces the effective diffusion distance can extend to several tip radii distances into the matrix. This implies that as the driving force decreases, effects further from the tip can influence the concentration field at the tip. Errors in the assumed boundary condition as a function of interfacial position will be more deleterious for small supersaturations. The model must be reviewed critically to ascertain what unrealistic assumptions are causing the theory to predict incorrect kinetics for low driving forces. In terms of the three dissipative processes, one must examine how each consideration might be in error with respect to the real situation as the interfacial position varies from the tip to the sides.

The diffusion equation itself has assumed a parabolic symmetry for the tip shape. If the parabolic symmetry is violated, then this would produce an error in the predictions. One particular case, where this is for certain invalid, is the growth of theta prime precipitates from Al-4% Cu. The thickness of these precipitates far
behind the tip is sometimes only several atom diameters, and the tips are observed to be somewhat squared off. Such a situation might be better described using circular symmetry than parabolic symmetry. When Hillert's (7) approximate theory for the circular symmetry is used and capillarity is ignored, the experimental and predicted values are closer to agreement. Hence, the disagreement between experiment and theory at low supersaturations may be due to the deviation from a parabolic shape. If the actual shape is more pointed than the parabola, then it would be expected from the point effect of diffusion that the actual kinetics would be faster than the parabolic prediction. This is generally the case shown in this work; the theory underestimates the kinetics if the driving force is low.

Another possible error in the theory is a deviation from isotropy in the surface energy. If the energy required for interfacial creation possesses a different dependence on interfacial position than assumed, then the predictions would be in error. This point has been discussed in detail in this chapter concerning the structure of the interface. The conclusion is drawn that, perhaps quantitatively, the assumed interfacial creation effect is in error due to the stepped nature of the interface; however, qualitatively the assumption is correct in the sense that interfacial creation would still play a greater role at the sharply curved, rapidly moving interfacial tip than at the flat, slowly moving sides. If the effect is overestimated at the tip or underestimated at the sides, the actual velocity would be faster than predicted. This effect may be appearing in
the discrepancy at low driving forces.

Finally, a third possible source of error in the theory is a strong anisotropy in interfacial mobility or some other undetermined interfacial process. If this interfacial process consumes more energy at the sides than at the tip, then the theory would underestimate the lengthening kinetics. The origin of the plate or needle shape is thought to be related to the immobile nature of the sides relative to the mobile nature of the tip. Thus, anisotropy in the interfacial mobility appears to be a reasonable effect to explore. Such an effect could rationalize the discrepancy between experiment and theory at low supersaturations.

In summary, comparison of the model with eleven different transformations has shown that in the cases where the supersaturation is large, the kinetics are reasonably rationalized. However, when the driving force is low, the experimental kinetics are typically faster than predicted. This suggests that the model is in error at low supersaturations. The expected reason for the error is the fact that conditions at the tip become sensitive to conditions at the sides for low driving forces. This results from the long effective diffusion distances which exist at low supersaturations. Three possible conditions at the sides were considered as possible contributors to the enhanced kinetics: (1) deviation from parabolic shape, (2) anisotropy in the interfacial energy or an improper treatment of the effect of interfacial creation, and (3) anisotropy in the assumed interfacial mobility or another undetermined interfacial process.
Conclusions

A number of Widmanstätten-type precipitates are examined in this thesis with respect to edgewise growth kinetics. The two transformations examined most closely are the precipitation of ferrite from austenite in pure iron-carbon alloys and the precipitation of alpha from beta copper-zinc alloys. The results of the study of these alloys have produced the following three basic conclusions concerning Widmanstätten transformations: (1) the kinetics are principally governed by solute diffusion in the matrix as assumed by the model of Trivedi; (2) the structure of the precipitate tip interface is semicoherent and stepped on an atomistic scale; and (3) deviation from interfacial equilibrium is predicted by the model, which is consistent with tip radii measurements and composition determinations.

The retardation of the Widmanstätten ferritic reaction is attributed to a thermodynamic effect which is consistent with the deviation from equilibrium proposed by Hillert (40). Although the concept of interfacial mobility may be responsible for the retarded kinetics, it is concluded that the notion of Hillert is more realistic. This conclusion is supported by the edgewise growth rates of upper bainite.

The enhanced edgewise growth kinetics of alpha precipitates in brass are principally caused by deviation from equilibrium in the precipitate. The model properly predicts the kinetics and tip radii if precipitate concentrations are assumed which are inconsistent with thermodynamic equilibrium but are consistent with experimental composition measurements.
A summary of the predictions of the model as compared to the experimental kinetics are shown in Table II for all eleven transformations considered in this research. The predicted kinetics are based on the assumption of interfacial equilibrium and a semicoherent interface for all the precipitates except molybdenum carbide. The molybdenum carbide results are predicted on the basis of an assumed disordered interface. An attempt is made in the table to correlate the predictions and measurements with several transformation characteristics including the matrix and precipitate structure, relative supersaturation, relative diffusivities in the two phases, bulk strain, and the type of solid solutions involved. In addition, the predicted change in interfacial solute concentration is compared with the change which would aid in relieving interfacial stresses.

No systematic correlation is seen between the kinetics and the bulk strain or the relative diffusivities. There is, perhaps, a dependence between the direction of the predicted deviation from equilibrium and the ability of the solute to relieve the interfacial stresses. Widmanstätten ferrite, which produces compressive strains, can be considered an example of this effect. If the carbon concentration at the interface in the matrix is reduced, the compressive strains are also reduced. This method of reasoning rationalizes all but three of the eleven transformations. The reasoning is, however, antithetical to the intuitive feeling that the transformation strains should always oppose the reaction.
Table 11. The kinetic results of this thesis are summarized. The observed kinetics are compared to the predictions for a semicoherent interface at equilibrium for all cases except molybdenum carbide. A disordered interface is predicted for molybdenum carbide. $\Omega_0$ greater than 0.3 is considered large.

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Matrix</th>
<th>Precipitate</th>
<th>Experimental Kinetics</th>
<th>$\Omega_0$</th>
<th>Strain</th>
<th>Predicted Change in Interfacial Composition Relieves Strain</th>
<th>Precipitate Diffusivity Relative to Matrix Diffusivity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe-C</td>
<td>$\gamma$(fcc)</td>
<td>Plate $\alpha$(bcc)</td>
<td>Slow</td>
<td>Large</td>
<td>Compressive</td>
<td>Yes</td>
<td>Fast</td>
</tr>
<tr>
<td>Steel</td>
<td>$\gamma$(fcc)</td>
<td>Upper bainite $\alpha$ + cementite</td>
<td>Slow</td>
<td>Large</td>
<td>Compressive</td>
<td>Yes</td>
<td>Fast</td>
</tr>
<tr>
<td>Steel</td>
<td>$\gamma$(fcc)</td>
<td>Lower bainite $\alpha$ + cementite</td>
<td>Slow</td>
<td>Large</td>
<td>Compressive</td>
<td>Yes</td>
<td>Fast</td>
</tr>
<tr>
<td>Steel</td>
<td>$\gamma$(fcc)</td>
<td>Plate cementite</td>
<td>Fast</td>
<td>Small</td>
<td>Compressive</td>
<td>Yes</td>
<td>Slow</td>
</tr>
<tr>
<td>Steel</td>
<td>$\alpha$(fcc)</td>
<td>Molybdenum carbide needle</td>
<td>Correct</td>
<td>Small</td>
<td>Compressive</td>
<td>No</td>
<td>Slow</td>
</tr>
<tr>
<td>Fe-N</td>
<td>$\alpha$(bcc)</td>
<td>Needle $\gamma$(fcc)</td>
<td>Fast</td>
<td>Small</td>
<td>Tensile</td>
<td>No</td>
<td>Slow</td>
</tr>
<tr>
<td>Cu-Zn</td>
<td>$\beta$(bcc)</td>
<td>Plate $\alpha$(fct) or fcc faulted</td>
<td>Fast</td>
<td>Large</td>
<td>Tensile</td>
<td>Yes</td>
<td>Slow</td>
</tr>
<tr>
<td>Cu-Zn</td>
<td>$\beta$(bcc)</td>
<td>Needle $\alpha$(fcc)</td>
<td>Fast</td>
<td>Large</td>
<td>Tensile</td>
<td>Yes</td>
<td>Slow</td>
</tr>
<tr>
<td>Cu-Zn</td>
<td>$\alpha$(fcc)</td>
<td>Plate $\beta$(bcc)</td>
<td>Fast</td>
<td>Small</td>
<td>Compressive</td>
<td>Yes</td>
<td>Fast</td>
</tr>
<tr>
<td>Al-Cu</td>
<td>$\alpha$(fcc)</td>
<td>Plate $\beta'(bcc)$</td>
<td>Fast</td>
<td>Small</td>
<td>Compressive</td>
<td>Yes</td>
<td>Fast</td>
</tr>
<tr>
<td>Ti-Cr</td>
<td>$\beta$(bcc)</td>
<td>Plate $\alpha$(hcp)</td>
<td>Slow</td>
<td>Large</td>
<td>Tensile</td>
<td>No</td>
<td>Slow</td>
</tr>
</tbody>
</table>
Molybdenum carbide is the only exception to the rule, that for small driving forces the model underestimates the measured kinetics. The failure of the model at small supersaturations is believed to result from the larger effective diffusion distance prevalent at low driving forces. The larger effective diffusion distances make the model more sensitive to interfacial assumptions behind the advancing tip. These assumptions relate to anisotropy in interfacial energy and interfacial mobility, and to the assumed precipitate shape.

The complete analysis presented in this thesis supports the following principal conclusions: (1) the edgewise growth kinetics of Widmanstätten precipitates are controlled mainly by volume diffusion, (2) the tip interface is semicoherent, (3) local equilibrium does not necessarily prevail at the interface, (4) the model of Trivedi should be revised to be more realistic for conditions of small supersaturations, (5) the Widmanstätten transformation is accomplished by a ledge mechanism, (6) local equilibrium does not necessarily prevail at the interface, and (7) the model of Trivedi should be revised to be more realistic for conditions of small supersaturations.

Recommendations for Further Research

The nature of science is such that research always begs further research. This work is no exception. Although this thesis has cleared up certain facets of the Widmanstätten problem relating to the validity of theoretical models and to the role of certain metallurgical phenomena during the transformation, it has also brought forth new problems for experimental and theoretical study.
Experimentally, there is a need to have more information concerning the actual shape and interfacial structure of the tips and sides of the Widmanstätten precipitates. In addition, microprobe data should always be available to determine if the crucial assumption of local equilibrium is valid. Empirical thermodynamic data is often lacking in the less common systems, which hinders the interpretation of the observed deviation from equilibrium.

The Widmanstätten transformation should be studied experimentally in its relation to the diffusionless massive transformation. It is observed in both brass and steel that the diffusional platelet transformation is replaced by a diffusionless massive transformation at large driving forces. Control of microstructure is contingent upon knowledge of such transitions. It would be fruitful to study the transition experimentally by observing the Widmanstätten transformation at large driving forces using pulsed heating and electron microscopy techniques.

The kinetics of Widmanstätten transformations could be studied under stress. If transformation stresses influence the deviation from equilibrium, then an externally applied stress may also affect the transformation. Kinetic data in addition to morphological, structural, and composition data taken from stressed samples would contribute to an improved understanding of the nature of the observed deviation from equilibrium.

Any experimental study of the Widmanstätten transformation should be comprehensive if it is to be analyzed on the basis of a theoretical
model. Four types of data should be taken to totally characterize the product: (1) in situ hot stage microscopy or an alternative indirect technique to determine the growth kinetics, (2) scanning electron microscopy to ascertain the precipitate shape, (3) transmission electron microscopy to reveal the precipitate and interfacial structure, and (4) electron microprobe data to establish empirically the deviation from equilibrium. This data together with an appropriate theoretical model presages what the transformation characteristics are and how they influence the growth of Widmanstätten precipitates.

An appropriate theoretical model should be consistent with the experimental observations and should be developed on the basis of sound mathematics and metallurgy. There is a need to develop a theoretical competence to support the various experimental observations. Primary emphasis has been placed on the diffusional lengthening kinetics, however these kinetics have been shown to be strongly influenced by other non-diffusional effects including morphology, interfacial structure, and deviation from local equilibrium. The present model treats volume diffusion rigorously for the given assumptions but lacks flexibility to account for slight variations in the assumptions. This difficulty originates from the complexity of the problem and is not easily ameliorated.

The theoretical approach should be extended to predict the precipitate shape and tip size. The shape is determined by volume diffusion, interfacial flux balance, interfacial structure, and perhaps many other effects which are not well understood theoretically. The present
shape assumption is justified empirically, however it should also be possible to arrive at a necessary shape from theoretical arguments. There already exists intense theoretical interest in predicting the size factor by invoking optimization principals, which assume that the tip radius is, in nature, a free variable which can adjust to a value so as to optimize some important physical quantity such as velocity, thermokinetic potential, rate of change of free energy, or entropy. The possibility that the actual Widmanstätten tip radius is not a freely varying parameter must be considered. The strong influence that interfacial structure and deviation from equilibrium has on the transformation intimates that these effects may preclude the utilization of an optimization principal, e.g., the actual tip radius may correspond to the maximum possible gradient in step density which could prevent the optimum radius from being realized.

Interfacial structure has been shown in this thesis to affect the kinetics of the Widmanstätten transformation through the effect on interfacial creation and the possible effect on observed deviation from equilibrium. The theory of phase boundaries, a field in itself, could be extended to interpret and predict the character of the Widmanstätten interface. This is a subject that perhaps theory could offer the best approach since the experimental observation of the tip interface is hindered by the small size of the tip and the inherent difficulties of observing structures having a dimension no larger than a single atom. The diffusional, elastic, and plastic interactions present at an interphase boundary are complex but nonetheless are
approachable. Interaction models undoubtedly will form an integral part of a realistic characterization of the Widmanstätten interface.

The assumption of local equilibrium across the interface has been seriously challenged by the present research. The magnitude of the apparent deviation from equilibrium has been estimated but could not be predicted independently from theory. The magnitude of the deviation is without physical meaning unless a model is available to interpret the data in terms of understandable concepts. More emphasis needs to be placed on the effects of stress and coherency on equilibrium and on interfacial migration. A better understanding of the theory of solid solutions is necessary, particularly, for the study of Widmanstätten transformations in systems where empirical thermodynamic data is either meager or nonexistent.

In conclusion, the recommendations for future research can be summarized as follows. Although the thrust of previous Widmanstätten kinetic studies has been made to be consistent rigorously with volume diffusion, it now seems necessary to transfer attention to the nature of the interface itself. This must be done with a minimal loss of the benefits of the rigorous volume diffusion model. Hence, the volume diffusion model is an appropriate starting point but fails to produce the final answers that the research seeks to obtain. The total characterization of the Widmanstätten transformation is contingent upon experiments revealing the growth kinetics, morphology, interfacial structure, and deviation from equilibrium. In addition, physical interpretation of the data can only be realized if models
are available to predict the observations from well known concepts such as diffusion, dislocations, and interfaces.
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APPENDIX: CALCULATION OF $e_\beta$

In Chapter V it is stated that Purdy's (42) calculation of the nonideal thermodynamic parameter, $e_\beta$, for zinc in the beta phase is in error. The present calculation is shown below in detail to support the reported value given in this thesis.

Purdy has used the following conventional definition of $e_\beta$ for zinc in the beta phase.

$$e_\beta = \left\{ 1 + \frac{\partial \ln \gamma_\beta}{\partial \ln c_\beta} \right\} c_\beta^o$$

($A1.1$)

$\gamma_\beta$ is the activity coefficient of zinc in the beta phase; $c_\beta$ is the concentration in mole fraction zinc in the beta phase; and $c_\beta^o$ is the equilibrium concentration of beta coexisting with alpha. Hultgren et al. (68) give the relationship between the activity coefficient and concentration as

$$\bar{F}_{Zn,\beta}^{xs} = RT \ln \gamma_\beta = -10520(1 - c_\beta)^2 + 420,$$

($A1.2$)

where $\bar{F}_{Zn,\beta}^{xs}$ is the excess free energy of zinc in the beta phase at 500°C or 733 K.

From Equation $A1.2$ it is seen that

$$\ln \gamma_\beta = -\frac{10500(1 - c_\beta)^2}{(1.98)(773)} + \frac{420}{(1.98)(773)}.$$  

($A1.3$)
Substitution of Equation A1.3 into Equation A1.1 and evaluation of the partial derivative gives

\[
e^o_B = \left[ 1 + \frac{21040(1 - c^o_B)c^o_B}{(1.98)(773)} \right] c^o_B.
\]

(A1.4)

\(c^o_B\) is 0.454 mole fraction zinc at 400°C. By letting \(c^o_B\) equal 0.454 and by calculating the necessary arithmetic, it is discovered that \(e^o_B\) is 4.41, not 13 as reported by Purdy. It is seen from Equation A1.4 that the nonideality is a function of the equilibrium interfacial concentration, \(c^o_B\). The nonideal thermodynamic parameter is 4.42 at 250°C and 4.39 at 500°C. The indirect dependence of \(e^o_B\) on temperature through \(c^o_B\) is weak, and 4.41 is considered a good value over the entire temperature range.