Deviation From Local Equilibrium During the Austenite to Ferrite Transformation in Steel

A Modelling Approach

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Abstract

This thesis highlights the role of phase interfaces on phase transformations in metallic materials. The deviation from local equilibrium at the moving phase interface has been analysed in terms of solute drag theory and finite interface mobility. In particular the planar growth of proeutectoid ferrite from austenite in steel has been studied. The deviation from local equilibrium is caused by dissipation of Gibbs energy by diffusion inside the phase interface and interface friction. In the analysis the interface is divided into three zones and the thermodynamic and kinetic properties are assumed to vary continuously across the interface. A new model suitable for multicomponent alloys is developed. The model reduces to the familiar solute drag model by Cahn under simplifying conditions.

It was demonstrated how the interface model could be combined with a method for calculating the volume diffusion in both the growing and parent phases. With this combination of procedures the changes in local conditions at the interface, as the growth rate changes due to long-range diffusion, could be demonstrated for the case of continuous cooling in an Fe-Ni alloy.

The critical limit for massive transformation in the Fe-Ni and Fe-C systems was calculated and found to lie well below the $T_0$ line for both systems. The calculated limit for Fe-Ni was compared with a recent experimental study and reasonable agreement was found. For the Fe-C system the limit calculated with the present model was compared with a phase-field model. The two approaches showed qualitatively the same behaviour and the quantitative difference was due to different assumptions on how properties vary across the interface.

Finally, an attempt to simulate the partitionless growth of ferrite in austenite in the Fe-Ni-C system was performed. In the applied model the dissipation of Gibbs energy inside the interface and in the nickel spike ahead of the migrating interface were accounted for. The long-range diffusion of carbon in austenite was treated with an approximate analytical growth equation. A continuous change from para-equilibrium conditions and quasi-paraequilibrium conditions could be shown in an isothermal section of the Fe-Ni-C phase diagram. Partitionless growth starts in a parabolic fashion but slows down. For alloys outside the limit for quasi-paraequilibrium partitionless growth is predicted to stop abruptly while for alloys inside that limit growth approaches a second parabolic growth law. However, the latter case should not be expected in practise because of impingement effects.

Keywords: Interface, Solute drag, Paraequilibrium, Simulation, Local equilibrium
Preface

The research presented in this thesis was carried out at the division of Physical Metallurgy, Department of Materials Science and Engineering, the Royal Institute of Technology (KTH) in Stockholm, Sweden.

This thesis is based on the following papers which will be referred to in the text by their roman numerals:

I  Comparison Between Solute Drag and Dissipation of Gibbs Energy by Diffusion
   M. Hillert, J. Odqvist and J. Ågren
   *Scripta Materialia* 45(2001)221-227

II The Phase-Field Approach and Solute Drag Modeling of the Transition to Massive $\gamma \rightarrow \alpha$ Transformation in Binary Fe-C Alloys
   I. Loginova, J. Odqvist, G. Amberg and J. Ågren

III Effect of Alloying Elements on the $\gamma$ to $\alpha$ Transformation in Steel. I
   J. Odqvist, M. Hillert and J. Ågren
   *Acta Materialia* 50(2002)3211-3225

IV A General Method for Calculating Deviation from Local Equilibrium at Phase Interfaces
   J. Odqvist, B. Sundman and J. Ågren

V On the Transition to Massive Growth During the $\gamma \rightarrow \alpha$ Transformation in Fe-Ni Alloys
   J. Odqvist
   *In manuscript*
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Chapter 1

Introduction

There is a direct correlation between how the atoms are arranged in a material and its chemical and physical properties. As an example, consider the change of magnetization in an ordinary stainless steel subjected to plastic deformation at room temperature. The deformation will change the atomic arrangement from one phase austenite, which is non-magnetic, to another structure martensite which is magnetic. The change from austenite to martensite is classified as a phase transformation and a method to study this transformation is actually to monitor the change in magnetization [1]. In the present thesis we will concentrate on the austenite to ferrite transformation, which usually is controlled by diffusion.

Due to the obvious economical advantages development of new materials, e.g. new steel grades, usually includes both modelling and experimental studies. The purpose of the experimental study is two-fold, firstly it will hopefully generate data for use as input to various computations supporting the development, secondly it will approve or disapprove some critical predictions of the theory supporting the development. Specifically, modelling of phase transformations require knowledge of thermodynamic and kinetic data to be successful. Storage and manipulation of experimental data soon becomes impossible without the use of computers. In the field of thermodynamics, this problem was recognised in the late 1960’s and since then numerous software for calculation of different thermodynamic quantities and even diffusion have been developed. Now, instead of focussing on the actual calculations, effort can be directed towards the important work of assessing new data and building databases.

An advanced software for calculation of phase equilibria and complex manipulation of thermodynamic quantities is Thermo-Calc [2,3], developed at KTH in Stockholm. Thanks to a graphical user interface and various interfaces for the application programmer Thermo-Calc is today a very powerful and versatile tool used by industry as well as universities world wide. For simulation of diffusion-controlled transformations the software DICTRA [4,3] has been developed at KTH and Max-Plack
Institute für Eisenforschung in Düsseldorf. DICTRA can treat diffusion in multi-component and multiphase systems and use Thermo-Calc for all thermodynamic calculations.

1.1 Modelling of phase transformations

In all models of complex phenomena it is necessary to introduce simplifications, some of which are more severe than others. Often, when modelling phase transformations in solid materials at sufficiently high temperatures one neglects the finite rate of heat conduction and changes in volume that may give rise to stresses and plastic deformation. It is simply assumed that the material has some effective way to level out temperature gradients and accommodate volume changes. For diffusion-controlled phase transformations in solid materials local equilibrium is usually assumed to hold at the phase interface between the growing and shrinking phase. Thus, for a binary alloy the boundary conditions for the diffusion problem can be evaluated directly from the phase diagram for the temperature under consideration.

![Figure 1.1](https://via.placeholder.com/150)

*Figure 1.1. Schematic phase diagram and composition profile illustrating the local conditions at the $\beta/\alpha$ phase interface at temperature $T_1$*
This is illustrated in Figure 1.1 which shows a schematic binary phase diagram for the A-B system where a $\alpha$ phase grows by diffusion into a $\beta$ phase at the temperature $T_1$. The composition profile below the phase diagram illustrate the local conditions at the phase interface between $\beta$ and $\alpha$. Furthermore, the interface is often assumed to be sharp without any specific properties. Although the described model for the local conditions at the interface is naive it is very useful [3] and the local equilibrium hypothesis, used already in 1889 by Stefan [5], is still much in use. However, it is well known that local equilibrium cannot prevail during certain phase transformations, i.e. there must be a deviation from local equilibrium. 

In order to model and predict phenomena where a deviation from local equilibrium is necessary, phase interfaces have been treated as thin regions with certain properties. In the simplest case the region constituting the interface is considered to have homogeneous properties over its width but more advanced models as the phase-field method use a more gradual change of properties over the interface. Thus, in the phase-field method the interface is considered to be diffuse. 

Interactions between solute atoms and migrating interfaces, considered important in recrystallisation and grain growth but also in phase transformations, are traditionally treated with the so-called solute drag theory. In solute drag models properties often vary continuously over the interface, but not to the same degree of sophistication as in the phase-field methods.

1.2 This thesis

From a practical point of view the austenite ($\gamma$) to ferrite ($\alpha$) transformation is undoubtedly one of the most important phase transformations in steel. Consequently, the different mechanisms by which austenite decompose have been an area of continuous research interest [6,7]. A topic of special interest, due to its influence on the hardenability of steel, has been the effect of alloying elements upon the rate of the austenite to ferrite transformation.

In the present thesis the planar growth of proeutectoid ferrite from austenite is studied with a model that accounts for the interaction between alloying elements and the moving phase interface, so-called solute drag. The solute drag is caused by dissipation of Gibbs energy due to diffusion inside the interface and interface friction. How the local conditions at the phase interface change during growth has been of special interest. The approach is a modelling one and the calculations have, where possible, been compared with experimental information from the literature. Nucleation, structural considerations of the interface and the detailed atomic mechanisms for interface movement, e.g. migration of ledges [8,9], will not be discussed. Throughout, thermodynamic and kinetic data from databases appended to the Thermo-Calc and DICTRA software, respectively, have been used.
Chapter 1. Introduction

In chapter 2 models, commonly referred to as solute-drag models, are discussed together with the model developed in the present work. Chapter 3 deals with the application of the new model to the austenite to ferrite transformation in steel. In chapter 4 some concluding remarks and suggestions for future work are given. Finally, the appended papers are briefly summarised in chapter 5 and the contribution to each of them from the present author is indicated.
Chapter 2

Solute drag and diffusional dissipation of Gibbs energy

The idea that solute atoms could have an effect on the rate of a reaction seems to have emerged during studies of recrystallisation in high-purity metals. When performing recrystallisation experiments on high-purity lead and lead with small amounts of impurities Beck [10] reported that the time of recrystallisation markedly increased for lead with added impurities. He found that by adding 0.0084 mass% Ag to high-purity lead the time of recrystallisation increased several thousand fold but he did not give any explanation for the observed phenomenon. Masing et al. [11] suggested that the impurities would have an tendency to segregate, presumably due to elastic interactions, to the grain boundaries and exert a retarding force on the moving grain boundaries. The grain boundary would have to drag an atmosphere of impurities along, which would result in considerably longer times of recrystallisation. Their ideas were developed in more detail in a paper by Lücke and Detert [12] which is considered to be the first quantitative theory of the impurity drag phenomenon, later called solute drag. Since then several other models for solute drag have been developed. Some of these will now be reviewed.

2.1 Cahn’s model

In 1962 Cahn [13] published his famous treatment of the impurity-drag effect in grain boundary motion. In his model the binding force between the solute atoms and the migrating grain boundary was derived and to get the total force acting on a unit area of the boundary, i.e. the pressure, he integrated over the width of the grain boundary, i.e.

\[ PV_m = - \int_{-\lambda}^{\lambda} (x_M - x_M^0) \frac{dE}{dy} dy \] (2.1)
Chapter 2. Solute drag and diffusional dissipation of Gibbs energy

Where $P$ is the total pressure acting to retard the motion of the boundary, $V_m$ is the molar volume, $x_M$ and $x_M^0$ are the mole-fractions of solute M inside the interface and far away from the grain boundary, respectively. The grain boundary half-width is denoted by $\lambda$, the interaction energy by $E$ and the perpendicular distance over the grain boundary is represented by $y$. As can be seen in Eq. 2.1 the term $x_M^0 \int dE$ will vanish for a one one-phase material and Cahn added this without any comments. In order to perform the integration in Eq. 2.1 the composition profile over the boundary has to be known. Cahn [13] applied the steady-state assumption to the diffusion equation and presented different analytical solutions for the high and low velocity limits. Furthermore, for simplicity he assumed a triangular shape of the interaction energy over the boundary. It could also be mentioned that Cahn, based on the 1962 treatment, later worked out a corresponding theory for phase transformations, but he never published the results [14]. Independently, Lücke and Stüwe [15] presented a theory very similar to the one by Cahn [13]. Their version of Eq. 2.1 was

$$PV_m = - \int_{-\lambda}^{\lambda} x_M \left( \frac{dE}{dy} \right) dy$$

Clearly, the only difference between Eq. 2.1 and Eq. 2.2 is the term $x_M^0 \int dE$. This is, as we will see later, a very important difference.

2.2 Hillert’s approach

When examining the effects of interfaces on phase transformations in the solid state Hillert [16] modelled the phase interface in binary alloys as a thin film of interface phase with its own Gibbs energy function. According to the model the movement of such an interface results in dissipation of Gibbs energy due to diffusion inside the interface and ahead of the advancing interface. In the model the thermodynamic and kinetic properties of the interface phase were kept constant over the width of the interface, thus allowing discontinuities at the interface with the growing and parent phase. Hillert compared the results from his model with the model by Cahn [13] for the case of a one-phase material and found good agreement. It could be mentioned that Hillert [17] already in 1960 had introduced the concept of dissipation of Gibbs energy for the action of an interface during a phase transformation.

Hillert and Sundman [18] developed Hillert’s approach [16] further and gave the following expression for the dissipation of Gibbs energy due to diffusion inside and ahead of the advancing phase interface in a binary substitutional alloy A-M

$$\Delta G_m^{diff} = - \frac{V_m}{v} \int_{-\infty}^{\infty} J \frac{d(\mu_M - \mu_A)}{dy} dy$$

where $v$ is the interface velocity defined as positive, $J$ is the interdiffusional flux and $d(\mu_M - \mu_A)/dy$ is the gradient of the diffusion potential for interdiffusion between
2.2. Hillert’s approach

A and M atoms. If steady-state conditions are assumed the interdiffusional flux $J$ can be written as [19]

$$J = \frac{v}{V_m} (x_M - x_{\alpha M}^\alpha) \quad (2.4)$$

where $x_{\alpha M}^\alpha$ is the mole-fraction of solute M in the growing phase $\alpha$. If we also assume that $x_{\alpha M}^\alpha = x_{\alpha M}^0$ Eq. 2.3 transforms to [19]

$$\Delta G_{\text{diff}}^m = -\int_0^\infty (x_M - x_{\alpha M}^0) \frac{d(\mu_M - \mu_A)}{dy} dy \quad (2.5)$$

In their treatment Hillert and Sundman [18] let the properties vary continuously between the two phases separated by the interface. As can be seen, Eq. 2.5 and Eq. 2.1 are similar and Hillert and Sundman were able to show that the two equations give the same result for a phase interface if the ideal solution model applies everywhere.

Much later, Purdy and Bréchet [20] and Enomoto [21] applied Eq. 2.1 to the austenite to ferrite transformation in Fe-X-C alloys, where X denote a substitutional alloy element, e.g. Mn, Ni. Both these authors showed calculated curves over solute drag as a function interface velocity seemingly starting from zero at low velocity. This is in contrast to the findings by Hillert and Sundman [18] where the corresponding curves started from a finite value at low velocity. This fact was later discussed by Hillert [19] and again together with detailed calculations by Hillert et al. (Paper I). Figs. 2.1 and 2.2 are taken from their paper. From Fig. 2.1 it is evident that the solute drag curves (when $\Delta E \neq 0$) do not start from zero at low velocities as claimed by Purdy and Bréchet [20]. Instead, the curves start from a value determined by the spike of alloy element M, pushed in front of the advancing

![Figure 2.1](image-url)

**Figure 2.1.** Dimensionless solute drag as a function of dimensionless velocity, plotted with a logarithmic scale for velocity, for the $\gamma \rightarrow \alpha$ transformation in an Fe-2%M alloy from Cahn’s equation, i.e. Eq. 2.1. $\Delta E$ is the difference in binding energy for solute M between the two phases. From **Paper I**.
Chapter 2. Solute drag and diffusional dissipation of Gibbs energy

interface. This spike will shrink as the difference in binding energy is lowered and completely disappear when $\Delta E = 0$, i.e. for a one-phase material, see Fig. 2.1. As discussed by Hillert et al. (Paper I) Eq. 2.1 and Eq. 2.5 evidently gives the same result despite the fact that the integration in the equations are carried out over different volumes.

Mathematically it is easy to show that equivalence between the two approaches holds if the Gibbs energy can be written as a sum of two functions, one which is a function of distance and one which is a function of composition. It may be less obvious what physical meaning this has. An exception is the case of an ideal solution where this condition is clearly obeyed. In Cahn’s model the spike does not contribute to solute drag because it only involves entropy of mixing and not the energy. In Hillert-Sundman’s Gibbs energy dissipation treatment also the entropy of mixing in the spike contributes to the total dissipation. However, the contribution in the interface is the same as in the spike but has the opposite sign and thus the two contributions cancel and the net result is the same as in Cahn’s treatment. From this it follows that it is very important over which volumes of material the driving force is evaluated because all dissipated energy needs to be accounted for by the available driving force.

\[ \text{Figure 2.2. Comparison of solute drag according to Cahn (Eq. 2.1) and Lücke and Stüwe (Eq. 2.2). From Paper I.} \]

So far we have not discussed the difference between Eq. 2.1 and Eq. 2.2. In Fig. 2.2 the solute drag from the two equations are compared for $\Delta E = RT$ and $\Delta E = 0$. As can be seen from Fig. 2.2 the two equations give the same result for a grain boundary but radically different result in the case of a phase interface. The difference arises from the extra term, $x_0^0 / M \int dE$, which will vanish for a grain boundary but not for a phase interface. In conclusion, Cahn’s model gives the same result as the dissipation approach for grain boundaries, and under simplifying conditions even for phase interfaces. The model by Lücke and Stüwe shows agreement with the dissipation approach only for grain boundaries.
2.3 The model by Odqvist et al.

The original solute drag theory and the diffusional dissipation of Gibbs energy approach were formulated for binary substitutional alloys and isothermal conditions and for simplicity they were based on ideal or regular solution thermodynamics. As already mentioned Cahn’s model has been extended to phase transformations and ternary systems [20,21] and a simplified version of the model by Hillert and Sundman [18] has also been developed [22–24].

In this section we will develop a general procedure, based on the model by Hillert and Sundman, for treating deviation from local equilibrium at phase interfaces caused by dissipation of Gibbs energy due to diffusion inside the interface and interface friction. In addition, it will be demonstrated how this procedure can be combined with a treatment of the volume diffusion in the growing and parent phase. The detailed description of the procedure can be found in Paper IV.

When working with alloys with both interstitial and substitutional solutes it is convenient to replace the ordinary molar content or mole fraction with the corresponding u-fraction. They can be related through the following expression

\[ u_k = x_k / \sum_j x_j \]  

(2.6)

where the summation in the denominator is performed only over the substitutional solutes, thus for alloys with substitutional solutes only, the u-fraction will equal the mole fraction. In order to calculate the composition profile over the interface we assume steady-state conditions and solve the following relation numerically

\[ (v/V_m)(u_k - u_{k}^{\alpha/\gamma}) = J_k - J_k^{\alpha} \]  

(2.7)

\( V_m \) is the molar volume per substitutional atom, \( v \) is the interface velocity and \( u_{k}^{\alpha/\gamma} \) denote the composition in the growing phase at the interface. For an alloy with \( n \) components there are \( n - 1 \) independent equations like Eq. 2.7. On the right-hand-side in Eq. 2.7 there is a difference in diffusional fluxes where \( J_k \) is the flux of \( n - 1 \) solutes over the interface given by the Onsager linear law of irreversible thermodynamics

\[ J_k = - \sum_{j=1}^{n-1} L_{k,j}'' \nabla \phi_j \]  

(2.8)

where \( \nabla \phi_j \) is the gradient in diffusion potential, i.e. the driving force for diffusion. The diffusion potential in Eq. 2.8 is given by

\[ \phi_j = \mu_j - \mu_n, \quad j = \text{substitutional solutes} \]  

(2.9)

and

\[ \phi_j = \mu_j, \quad j = \text{interstitial solutes} \]  

(2.10)

where \( \mu \) is the ordinary chemical potential. Element \( n \) is an arbitrarily chosen substitutional element and is usually taken as the major element, i.e. the solvent in a
Chapter 2. Solute drag and diffusional dissipation of Gibbs energy

dilute solution. As can be seen in Eq. 2.7 the composition profile over the interface
is influenced by the diffusional flux, \( J_k^\alpha \), in the growing phase as suggested recently
by Hillert et al. [25]. The diffusional fluxes in Eq. 2.8 is defined so that their sum
for substitutional solutes vanishes, i.e. \( \sum J_k = 0 \). The kinetic parameters \( L'' \)
in Eq. 2.8 can be related to the individual diffusional mobilities for each solute, see
e.g. Ref. [26] for details.

In order to perform any calculations it is necessary to have a detailed description of
how the thermodynamic and kinetic properties vary over the interface. Following
Hillert and Sundman [18] we divide the interface into three zones. For simplicity,
a linear variation of the thermodynamic properties and of the logarithm of the in-
dividual diffusional mobilities is assumed over each zone. For further details, see
Paper IV.

The dissipation of Gibbs energy due to diffusion inside the interface is now evaluated
from the following equation.

\[
\Delta G_{m}^{\text{diff}} = -\frac{V_m}{v} \sum_{k=1}^{n-1} \int J_k \frac{\partial \phi_k}{\partial y} dy
\]  

(2.11)

The integration is performed over the thickness of the interface and Eq. 2.11 gives
the dissipation per mole of substitutional atom of the growing phase. Furthermore,
the dissipation is defined positive for a spontaneous reaction. Clearly, Eq. 2.11 is
a more general form for the dissipation than Eq. 2.5. There are two reasons why
the integration in Eq. 2.11 is only performed over the interface, not including the
solute spike as in Eq. 2.5. Firstly, when considering alloys with at least one fast
diffusing interstitial solute, e.g. carbon in Fe-X-C alloys where X represents a sub-
stitutional alloy element with very sluggish volume diffusion, it would be a good
approximation to assume a constant carbon activity over the interface and over
the spike of X as long as the interface velocity is not too high. At high velocities
this approximation will not be valid. Secondly, when considering non-steady-state
cases the diffusion problem in the parent phase does not need to be solved before
the dissipation calculation, thus making the interface model more easy to combine
with e.g. the DICTRA software.

At high interface velocities the Gibbs energy dissipation due to friction of the in-
terface should dominate and is given by

\[
\Delta G_{m}^{\text{friction}} = \frac{v}{M} V_m
\]  

(2.12)

where \( M \) is the interface mobility. Different expressions have been suggested for
the interface mobility. Here we will assume that \( M \) is composition independent and
have a temperature dependence of the form \( M = M_0 e^{Q/RT} \), where \( Q \) is the
activation energy, \( R \) denote the gas constant and \( T \) the absolute temperature. As
the dissipation is only evaluated over the interface so should also the driving force. The driving force acting on the interface is given by

$$\Delta G_{tot}^m = \sum_{k=1}^{n} u_{k}^{trans} \Delta \mu_k$$

(2.13)

where $\Delta \mu_k$ is the difference in chemical potential for all components on each side of the interface. Hillert et al. [25] derived expressions for how the driving force should be modified if diffusion in the growing and parent phase was taken into account. They suggested the following expression for the mole fraction of component $j$ transferred across the interface [25].

$$x_j^{trans} = \frac{(x_j^\alpha J_j^\gamma - x_j^\gamma J_j^\alpha)/(J_j^\gamma - J_j^\alpha)}{J_j^\alpha - J_j^\gamma}$$

(2.14)

Transforming each $x_j^{trans}$ with Eq. 2.6 gives the corresponding $u$-fraction $u_{k}^{trans}$ used in Eq. 2.13. $J_i^\alpha$ and $J_i^\gamma$ represents the diffusional fluxes in the growing phase $\alpha$ and parent phase $\gamma$, respectively.

For a constant interface velocity and steady-state over the interface possible growth conditions is found by balancing the total dissipation inside the interface with the driving force across the interface, i.e. from Eqs. 2.11, 2.12 and 2.13 we get

$$\Delta G_{tot}^m = \Delta G_{m}^{diff} + \Delta G_{m}^{friction}$$

(2.15)

Figure 2.3. Illustration of the energy balance in Eq. 2.15 represented by the two black dots. From Paper II
The typical shapes of the dissipation and driving force curves as a function of interface velocity can be seen in Fig. 2.3 where two possible growth conditions are denoted by black dots. The solid curve represents the right-hand-side in Eq. 2.15 and the dashed curve the left-hand-side.

The general coupling of the interface procedure described above with a method to calculate the diffusion in $\alpha$ and $\gamma$ can be made with the following flux balance equations

$$\left(\frac{v}{V_m}\right)(u_{k}^{\gamma/\alpha} - u_{k}^{\alpha/\gamma}) = J_{k}^{\gamma} - J_{k}^{\alpha}$$

For an alloy with $n$ components we will have $n - 1$ flux balance equations like Eq. 2.16. However, we have $2n - 1$ unknowns, i.e. the velocity $v$ and the $2(n - 1)$ contents, $u_{k}^{\gamma/\alpha}$ and $u_{k}^{\alpha/\gamma}$, on each side of the interface. Thus, to get a unique solution we need $n$ more conditions. These conditions usually comes from the $n$ thermodynamic conditions that ensure local equilibrium at the phase interface as in e.g. DICTRA. It is now suggested that these $n$ conditions are replaced by the $n - 1$ conditions obtained after integrating Eq. 2.7 over the interface and the single condition given by Eq. 2.15, thus resulting in $n$ conditions.

### 2.4 Discussion of model assumptions

As is evident from the previous section several assumptions have been introduced when developing the solute drag theory. For example, it is assumed that steady-state conditions could be maintained over the interface. This condition may not be fulfilled in the general case if long-range diffusion is present. On the other hand, since the interface width is so much smaller than the rest of the system one may argue that the steady-state assumption is a very good approximation [25].

Since the precise variation of the thermodynamic and kinetic properties over the interface is not known every choice made may seem more or less ad hoc. This serious drawback is common to all solute drag models and even the more advanced phase-field method. In order for the solute drag theory to have any predictive power more experimental data are needed. For example, solute drag models consider the trans-interface diffusivity while experimental data available usually considers the diffusivity along grain boundaries and phase interfaces. Due to the fact that interfaces are very thin it is hard to see how the trans-interface diffusivity ever will be a quantity explicitly measurable. Instead, many of the parameters present in solute drag and phase-field models will have to be measured in an indirect manner e.g. by fitting experimental temperature dependencies of growth rates.

In Eq. 2.15 it is assumed that only two sinks for Gibbs energy exists: one due diffusion inside the interface and the other due to the interfacial friction. Of course, more dissipative terms could have been added e.g. the interfacial energy. In fact, during the derivation it was tacitly assumed that the interface is planar, i.e. an
2.4. *Discussion of model assumptions*

infinite radius of curvature was assumed. However, the effect of a finite radius of curvature can be introduced implicitly through the DICTRA software. Finally, it should be emphasised that all solute drag models are one-dimensional and thus strictly valid only if sidewise diffusion could be neglected, which may be a good approximation for partitionless transformations but not in general, e.g. during growth of sharp needle-like crystals.
Chapter 3

Austenite to ferrite transformation in steel

As already mentioned in section 1.2, the austenite to ferrite transformation in steel is of great practical importance and has been studied extensively both experimentally and theoretically. Many studies have focused on the diffusion-controlled decomposition of unalloyed as well as alloyed austenite into products like proeutectoid ferrite or cementite, pearlite and bainite, each with its own morphology. For a long time metallurgists have tried to predict from theory this microstructural evolution. Of special interest is how the rate of the transformation is influenced by different alloy elements. In this context the change of the local conditions, e.g. deviation from local equilibrium, at the phase interface becomes important.

In this chapter we discuss the application of the model by Odqvist et al. developed in section 2.3 to the austenite to ferrite transformation in Fe-X, Fe-C and Fe-X-C alloys, where X is a substitutional element, e.g. X=Ni, Cr, Mn, Mo, and C represents carbon.

3.1 Fe-X and Fe-C alloys

It is well known that the volume diffusivity of substitutional alloy elements in iron-based alloys is very sluggish, even at relatively high temperatures. This means that the diffusion-controlled austenite to ferrite transformation in these alloys is very slow. However, experimental studies of the austenite to ferrite transformation in e.g. binary Fe-Ni shows that the growth of ferrite can proceed at a much higher rate than under diffusion-controlled growth if only the partitioning of nickel between austenite and ferrite could be avoided [27–38]. Transformations without long-range diffusion and partitioning of alloy elements are called partitionless transformations. There are basically two types of partitionless transformation: the massive and martensitic one. The martensitic transformation is considered not only
partitionless but also diffusionless. In this section we will only discuss the massive phase transformation.

Already in 1930, when investigating the $\beta \rightarrow \alpha$ transformation in Cu-Zn alloys, Philips [39] found that $\alpha$ could grow with the same composition as the parent $\beta$ and in the optical microscope it seemed as $\beta$ had transformed “as a unit” into $\alpha$. Greniger [40] described the morphology as “massive $\alpha$” and called the transformation a “mass transformation”. Today, the suggested definitions of a massive transformation includes its partitionless nature and the blocky or massive morphology. There are still controversies concerning the role of orientation relationships between parent and product phases during nucleation and growth of massive products [41].

Thermodynamically a partitionless transformation is only possible below the temperature ($T_0$) where Gibbs energy of the two phases is equal. The locus of all such temperatures is usually referred to as the $T_0$ line. The critical limit where the massive transformation is kinetically possible has been experimentally determined for the Fe-Ni system under isothermal conditions [37] as well as during continuous cooling [33,36]. In order to model the critical limit for massive transformation the model needs to account for properties such as interface mobility and the diffusional mobility of atoms inside the interface [42]. As we have seen in chapter 2 the solute drag theory offers these possibilities. Many attempts to model the massive transformation with solute drag theory have been published in the literature [22-24,43-47].

![Figure 3.1. Critical composition for massive growth in the Fe-Ni system. Experimental points are from Ref. [37]. The dashed lines are calculated with a different diffusivity in the interface, a factor of 10 higher in (a) compared to (b). From Paper III.](image-url)
Recently, Borgenstam and Hillert \[37\] measured the critical limit for the massive
austenite to ferrite transformation in Fe-Ni by isothermal heat treatment of diffusion
couples. Their results can be seen in Fig. 3.1 (symbols) which is a part of the
binary Fe-Ni phase diagram with the $T_0$ line superimposed. Included in Fig. 3.1 is
also a calculation of the critical limit (dashed line) due to Odqvist et al. (Paper
III). The agreement between experimental data and calculations in Fig. 3.1 could
be considered reasonable given the great uncertainty in many of the model param-
eters, e.g. diffusivity of nickel in the interface and its temperature dependence.

Most of the previous attempts to model the massive transformation have only
considered isothermal conditions. An exception is the work by Enomoto \[47\] in
which a solute drag model was used to simulate the diffusion-controlled and mas-
sive growth of ferrite in austenite for an Fe-Mn alloy (with a low carbon content)
and for low-carbon iron alloys during continuous cooling. Another example is the
work by Odqvist (Paper V) where a newly developed procedure (Paper IV)
treating the dissipation of Gibbs energy due to diffusion was combined with the
DICTRA software [4,3]. The new calculation package was applied to the austenite
to ferrite transformation in an Fe-6 at% Ni alloy and to the transition to massive
growth of ferrite during continuous cooling. Odqvist was able to show how the local
conditions at the phase interface gradually changed when the growth rate changed
with time as a result of the volume diffusion in both the growing and parent phase.
The results for continuous cooling is shown in Fig. 3.2. Two different cooling rates
were used and it is clear that the compositions at the interface ($x_{\alpha/\gamma}^{\alpha/\gamma}$ and $x_{N\gamma}^{\gamma}$)
deviates from the corresponding compositions when assuming local equilibrium at

\[ \begin{align*}
\text{Figure 3.2. A part of the binary Fe-Ni phase diagram with the } T_0 \text{ line super-
imposed. The alloy composition is represented by the dashed line. The curved}
\text{lines shows how the interface composition vary during continuous cooling with two}
\text{different cooling rates. From Paper V.}
\end{align*} \]
Chapter 3. Austenite to ferrite transformation in steel

the interface. If local equilibrium were to hold at the interface the compositions would follow the \( \alpha/\alpha + \gamma \) and \( \gamma/\alpha + \gamma \) phase boundaries at all times. As can be seen in Fig. 3.2 the calculations predict a sudden transition to massive transformation at 903 K and 942 K for a cooling rate of 0.1 K/s and 1 K/s, respectively.

![Figure 3.3](image.png)

**Figure 3.3.** Calculated Fe-C phase diagram with the \( T_0 \) line superimposed. Curves \( a \) and \( b \) are the critical compositions from phase-field simulations using different choices of the interface mobility. Curve \( c \) is the critical composition from solute drag simulations. The two stars (*) denote experimental data from Morozov [48]. From Paper II.

Finally, an attempt to determine the critical limit for the massive \( \gamma \) to \( \alpha \) transformation in Fe-C should be mentioned. Loginova et al. (Paper II) compared simulations from a phase-field method with the predictions from a solute drag model. Fig. 3.3 is from their paper and shows the critical limit for massive transformation calculated with a phase-field method (curve \( a \) and \( b \)) and a solute drag model (curve \( c \)). Loginova et al. concluded that the two approaches qualitatively show the same behaviour and that the quantitative difference is due to a different variation of the properties across the interface. The interface is simply more diffuse, thanks to the so-called phase-field variable, in the phase-field method compared to the solute drag model.

Two experimental points, denoted by stars (*), are also included in Fig. 3.3 and these are from a study by Morozov [48]. As can be seen in Fig. 3.3, the agreement is very good for curve \( a \) at 1050 K. At higher temperatures Morozov’s measurements seems to indicate a faster approach to the \( \alpha \) one-phase boundary than predicted by solute drag and phase-field calculations. For lower temperatures, Morozov’s next data point is at 925 K and the critical composition is found to be 0.014 (not shown in Fig. 3.3) [48]. This comparison between theory and experiment emphasise the great uncertainty in the model parameters in both the solute drag and phase-field models.
3.2 Fe-X-C alloys

As already mentioned in section 1.1 local equilibrium is often assumed to prevail between two phases separated by a migrating interface in a solid state phase transformation. However, for alloys with both a fast diffusing interstitial solute and a slow diffusing substitutional solute, e.g. Fe-X-C, local equilibrium at the phase interface is not necessarily fulfilled. The transformation rate in these alloys are often controlled by diffusion of carbon in the parent phase while the alloy element (X) could be considered immobile. This was realised already in 1947 by Hultgren [49] when studying the transformation of austenite in alloyed steels. When Hultgren compiled his kinetic data they could often be represented with two C-shaped curves in the TTT-diagram instead of one, thus indicating that two modes of formation of austenite decomposition products were operating. Since Hultgren also found that the product phases sometimes formed with the same alloy content as the parent phase he concluded that the unexpected appearance of the TTT-diagrams were due to the behaviour of the alloying elements during the transformation. He introduced the prefix *para* and called the products paraferrite, paracementite and parapearlite and the local condition at the phase interface during growth of these products was named paraequilibrium [49]. Thus, paraequilibrium is characterised by a constant carbon activity across the interface but the same alloy content in the growing and parent phase. When discussing Hultgren’s paraequilibrium concept Hillert [51]

![Figure 3.4. Isothermal section in an Fe-X-C alloy illustrating quasi-paraconditions (NPLE).](image)

pointed out that the transformation could proceed under full local equilibrium but then there would be a spike of substitutional solutes, being pushed ahead of the migrating interface. The conditions at the interface for this case was later referred to as quasi-paraconditions by Hillert [52], but the name in most use today is nonpartitioning local equilibrium (NPLE). In Fig. 3.4 and Fig. 3.5 the two concepts are illustrated for an Fe-X-C alloy. It should be emphasised that paraequilibrium and quasi-paraconditions should be considered as limiting cases and in reality conditions should fall somewhere in between. In a recent paper by Oi et al. [53] the
kinetic boundary between partitioned and unpartitioned growth of proeutectoid ferrite in austenite in Fe-Mn-C and Fe-Ni-C alloys were studied experimentally. They concluded that the kinetic boundary lies significantly outside the calculated limit for quasi-paraconditions but well inside the calculated paraequilibrium limit. They postulated a solute-drag effect as responsible for the observed results. Inspired by the work by Oi and co-workers Odqvist et al. (Paper III) presented an attempt to model the transition between paraequilibrium and quasi-paraconditions during planar, partitionless growth of proeutectoid ferrite in an Fe-Ni-C alloy. Odqvist et al. studied the local growth conditions at the interface by balancing the dissipation with the driving force, see section 2.3. They were able to show a continuous change
from paraequilibrium to quasi-paraconditions in the isothermal section of the phase diagram, see the thick solid line between points $P$ and $F$ in Fig. 3.6. The diffusion of carbon in the austenite was treated with a simple, approximate equation for planar growth. Partitionless growth was predicted to start in a roughly parabolic fashion but slows down. For alloys outside the limit for quasi-paraconditions partitionless growth is predicted to stop abruptly while for alloys inside that limit growth approaches a second parabolic growth law. However, the latter case should not be expected in practise due to impingement effects.

It should also be mentioned that the transition between paraequilibrium conditions and quasi-paraconditions for a number of Fe-Ni-C alloys has recently been studied experimentally and theoretically by Hutchinson et al. [54]. They developed a special model for the build-up of the nickel spike in front of the advancing interface and were able to show how the local conditions at the interface changes gradually when the growth rate changes gradually during growth. Their model could be considered to be a sharp interface model based on a comparison of the relative times it takes for a nickel atom and the interface to move a distance equal to the width of the interface. In their model Hutchinson et al. emphasise that they do not consider any dissipation of Gibbs energy inside the nickel spike which is in contrast to Odqvist et al. (Paper III), but the net result from the two approaches are however in qualitative agreement.

Ever since the pioneering work by Hultgren an impressive amount of research has been devoted to the study of the effect of different alloying elements on the transformation of austenite. It would be impossible to comment on all the important work done is this very lively field of research, instead the reader is referred to a recent review by Aaronson and co-workers and the extensive list of references found therein [55].
Chapter 4

Concluding remarks and suggestions for future work

From the preceding chapters it could be concluded that the solute drag theory certainly offers reasonable predictions of the influence of alloying elements on the rate by which proeutectoid ferrite grows in austenite even though more experimental work, designed to facilitate the comparison with the theory, needs to be performed. Successful predictions however relies partly on that the theory is treated in a rigorous way but also that the physically based model parameters are reasonably well known. The latter is one of the main weaknesses with the solute drag theory. The variation of thermodynamic and kinetic properties over the grain boundary or phase interface are unfortunately not known and as discussed in many of the appended papers this variation is crucial for the outcome of a simulation. This problem with the solute drag theory is shared by the very popular phase-field method.

Furthermore, the solute drag theory is inherently one-dimensional and can strictly only be applied to partitionless transformations in which sidewise diffusion could be neglected with good approximation. This is in contrast with the phase-field method which is easy to apply in several dimensions. Accordingly, the result from a phase-field simulation can often be presented as very realistic pictures of microstructural evolution e.g. dendrite and Widmanstätten formation and growth. On the other hand, calculations with the phase-field method is far more computer demanding compared to calculations performed with the solute drag theory.

In section 2.3, and in more detail in Paper IV, the model used in the present thesis was described. It is based on the evaluation of the dissipation of Gibbs energy by diffusion inside the interface and the corresponding driving force. However, when accounting for the long-range diffusion in both the growing and parent phase Gibbs energy will be dissipated due to the diffusion necessary for adjusting the composition of the material transferred across the interface and it is by no means
obvious how to separate these two energy sinks. This was recently discussed by Hillert et al. [25] when analysing the local conditions at the phase interface during diffusion-controlled phase transformations. They emphasised the relation between solute drag and dissipation of Gibbs energy by diffusion and argued that the dissipation approach would be more general because diffusion in the adjacent phases is possible even though the interface is not moving.

In the immediate future the model described in section 2.3 should be applied to ternary alloys of the Fe-X-C type to further investigate transitions between different local conditions at the interface. With the present coupling of the model to DICTRA it would be of interest to also study the transformation behaviour during continuous cooling for Fe-X-C alloys.

Recently, Ma et al. [56] introduced gradient thermodynamics into a continuum model of grain boundary segregation and showed how the gradient energy could play an important role for the outcome of simulations with solute drag models. Thus, it would be of great interest to introduce a gradient energy term in the present model. Such a term, proportional to the square of the gradient of the phase-field variable, is usually included in phase-field models.

As already mentioned, the difficulties to directly measure many of the model parameters makes it necessary to try to relate and fit these parameters against available experimental information such as growth rates.
Chapter 5

Summary of appended papers

5.1 Paper I

Comparison Between Solute Drag and Dissipation of Gibbs Energy by Diffusion.

In this paper numerical calculations of the solute drag and dissipation of Gibbs energy in a partitionless phase transformation are compared and discussed. It is concluded that the two approaches give the same result if the solute drag is compared with the driving force over the interface and the solute spike in front of the advancing interface. Furthermore, the solute drag models due to Cahn [13] and Lücke and Stüwe [15] are compared and it is found that the model by Cahn should be used in the case of a phase transformation.

The present author implemented the models, performed the calculations and contributed to the discussion.

5.2 Paper II

The Phase-Field Approach and Solute Drag Modeling of the Transition to Massive $\gamma \rightarrow \alpha$ Transformation in Binary Fe-C Alloys.

This paper was initiated by Ågren, Loginova and Amberg to investigate the application of a phase-field method to the massive autenite to ferrite transformation in binary Fe-C alloys. The paper was extended with a comparison of a solute drag model and phase-field method. It was found that the two approaches show qualitatively the same behaviour and that the quantitative difference stems from different assumptions on how properties vary across the phase interface. Both approaches
Chapter 5. Summary of appended papers

predicts a transition to a massive transformation at a critical temperature, below $T_0$ and close to the $\alpha/\alpha + \gamma$ phase boundary.

The present author performed the solute drag calculations, wrote parts of the paper and contributed to the discussion of the results.

5.3 Paper III

Effect of Alloying Elements on the $\gamma$ to $\alpha$ Transformation in Steel. I.

This paper is an attempt to simulate the partitionless growth of $\alpha$ in $\gamma$ of Fe-Ni-C alloys. A new procedure was developed to account for the solute drag by evaluating the dissipation of Gibbs energy due diffusion inside the interface and in the nickel spike being pushed in front of the advancing interface. The diffusion of carbon in $\gamma$ was treated with an approximate analytical growth equation while diffusion in $\alpha$ was neglected. A continuous change from paraequilibrium to quasi-paraconditions (NPLE) at the phase interface could be illustrated in the phase diagram. The simulation results were compared with a recent experimental study by Oi et al. [53].

The present author implemented the new procedure, performed all calculations and contributed to the discussion of the results.

5.4 Paper IV

A General Method for Calculating Deviation from Local Equilibrium at Phase Interfaces.

This paper deals with the description of a general method to calculate deviation from local equilibrium at phase interfaces in multicomponent systems. In the method the local equilibrium conditions between two solution phases are replaced by steady-state diffusion equations. Relations between the local contents on each side of the phase interface and the migration rate are derived and a condition in which the available driving force over the interface is balanced by the dissipation of Gibbs energy due to interface friction and diffusion inside the interface is introduced. It is also shown how this method straightforwardly can be combined with a software, e.g. DICTRA, to calculate the diffusion in adjacent phases.

The present author performed the implementation, calculated the diagrams and wrote parts of the paper.
5.5 Paper V

On the Transition to Massive Growth During the $\gamma \rightarrow \alpha$ Transformation in Fe-Ni Alloys.

This paper is the first application of the coupling, described in Paper IV, between a solute drag model and the DICTRA software. The austenite to ferrite transformation in Fe-Ni alloys and the transition to a massive transformation upon cooling is studied. It is shown how the local conditions at the phase interface gradually changes as a result of diffusion in both austenite and ferrite as well as inside the interface.

The present author did all the work
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