PHASE TRANSFORMATIONS IN HETEROGENEOUS STEELS

by

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- A first rate theory predicts; a second rate theory forbids, and a third rate theory explains after the event.

A. I. Kitaigorodskii, Quoted A. L. Mackay,

“Harvest of A Quiet Eye”
* To the present, past and future inhabitants of “Bait-ul-Amin”......my home.
This dissertation, which is submitted for the degree of Doctor of Philosophy in the University of Cambridge, describes research carried out under the supervision of Dr. H. K. D. H. Bhadeshia in the Department of Materials Science and Metallurgy, Cambridge, between April 1986 and January 1990. Except where acknowledgement, and reference to previous work has been made, this work is, to my best knowledge, original and has been done without collaboration. Neither this dissertation, nor any one substantially similar to it has been or is being submitted for a degree, diploma or other qualification at any other University. This dissertation consists of less than sixty thousand words.

Shahid Amin Khan,

February, 1990.
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1.1 Introduction

It is the primary aim of the present work to investigate the effect of chemical segregation in austenite on its transformation to different phases. These phases may vary not just in morphology, but in transformation mechanisms, phase compositions, crystallographic structure and thermodynamic stability. This literature survey is intended to describe the morphologies of different microstructures and to summarise their transformation mechanisms where they are known.

Castings and weld deposits both usually experience three major transformations during the course of their manufacture:

1. liquid to solid transformation, with the product phase being either primary austenite (γ) or delta ferrite (δ);
2. transformation of delta ferrite to austenite if this is not the primary solidification phase;
3. further decomposition of austenite to a variety of transformation products such as allotriomorphic ferrite, Widmanstätten ferrite, bainitic ferrite and martensite.

The chemical segregation of substitutional solutes can occur on a relatively major scale during transformations (1) and (2), but this can subsequently influence the transformations described in (3).

1.2 Liquid to Solid Transformation

The fundamental principles of the solidification of cast metals are now very well understood\(^1\,^2\) and attempts have been made to apply\(^3\,^4\) them to the study of weld pool solidification. The situation in welding is more complicated due to the movement of the heat source so that melting, mixing and freezing occur at different points within the same pool and the direction of maximum heat flow varies with time during solidification, so that the simplified one dimensional approximations valid for ingot solidification do not always hold for welding situation. It is intended to present here a brief comparison of ingot and weld pool solidification.
Nucleation, particularly, heterogeneous nucleation is the norm in ingot solidification and the formation of chill, columnar and equiaxed microstructure is observed. In weld pool solidification no nucleation stage is involved and continuity of grains exists across the HAZ/fusion zone interface\textsuperscript{[5,6]}. The absence of equiaxed microstructure in welds is due to the very severe thermal conditions in the melt. Generally the weld pool volume is small compared with the surrounding components, which act as a huge heat sink, and, along with low heat input give rise to very large thermal gradients, rapid cooling and hence stresses. A reasonably constant thermal gradient exists during ingot solidification. Only slight turbulence is experienced by an ingot depending on pouring conditions but electromagnetic stirring of the weld pool generated by Lorentz forces create conditions of considerable turbulence with in the pool\textsuperscript{[7]}. 

1.3 Decomposition of Austenite

When austenite is rapidly cooled to a very low temperature, there may not be enough time or atomic mobility to facilitate the reconstructive formation of ferrite. Under this circumstances, Widmanstätten ferrite, bainite or martensite can be produced depending on the level of the undercooling. In contrast, when specimens are cooled to relatively high temperature below $A_{e3}$, the austenite phase can undergo complete reconstruction into the ferrite phase. The key characteristics of phase transformations in steels have been summarised by Bhadeshia\textsuperscript{[8]}

1.3.1 Allotriomorphic Ferrite

The layer like shape of this phase is such that it does not reflect the symmetry of its crystal structure. The other terms such as grain boundary ferrite, polygonal ferrite and proeutectoid ferrite are too general and fail to distinguish between Widmanstätten ferrite and allotriomorphic ferrite, both of which can form above the eutectoid temperature and at austenite grain boundaries.

The allotriomorphic ferrite usually nucleates at the austenite grain boundaries. The classical view\textsuperscript{[9,10]} is that transformation occurs with $\alpha$ nuclei forming a partially coherent interface with atleast one of the adjacent austenite grains, while a random relation exists with the other. The partially coherent interface is then believed to move
Fig. 1.1: Schematic representation of the grain boundary nucleation of allotriomorphic ferrite and Widmanstätten ferrite.

by the displacement of ledges; while the other relatively high energy interface is supposed to be displaced by the continuous motion of the whole interface in a direction normal to itself. According to Hillert\cite{11}, a ferrite nucleus can have rational orientation relationships with both the adjacent austenite grains in some cases if crystallographic texture in the austenite permits it. Further growth is usually extremely rapid in low-alloy steels, with the allotriomorphic ferrite forming almost continuous layers along the $\gamma$ grain boundaries as shown in Fig. 1.1. The kinetics of growth of allotriomorphic ferrite are very important to models of microstructure prediction, as the fraction of ferrite determines the volume fraction of austenite available to subsequently form the other phases and also the degree of carbon enrichment of the remaining austenite. Allotriomorphic ferrite is perceived as being detrimental to the toughness. Its continuous layer morphology provides minimal resistance to crack propagation\cite{12,13}. 


1.3.2 *Widmanstätten Ferrite*

Widmanstätten ferrite forms in a temperature range where reconstructive transformation becomes relatively sluggish and gives way to displacive transformations. It has the shape of a thin wedge (Fig. 1.2), the actual shape being somewhere between that of a plate and a lath*. The displacive transformation mechanism should cause the generation of a large strain energy, incompatible\[^{14}\] with the low undercooling below the $A_{\text{e}3}$ temperature where $\alpha_W$ forms, but is largely eliminated by the simultaneous formation of two back-to-back self accommodating plates, as shown in Fig. 1.2, whose shear displacements cancel to a large extent. The characteristic wedge shape is a consequence of the slight misorientation of the habit planes of these two variants. Both the adjacent variants of Widmanstätten ferrite plates have been known to possess a Kurdjumov-Sachs type orientation relation with the parent austenite\[^{15}\].

Because $\alpha_W$ forms at lower undercoolings, the diffusion of carbon during growth is a thermodynamic necessity. However, the growth rate of Widmanstätten ferrite ($\alpha_W$) is higher than would be expected from the diffusion controlled motion of carbon planar interface because multidirectional diffusion occurs at the tip compared with unidirectional diffusion ahead of a plane boundary as shown in Fig. 1.3. The displacive nature of this product means that the effect of alloying elements such as Mn, Ni and Cr is less than for allotriomorphic ferrite. At high alloying levels the temperature at which $\alpha_W$ can form is depressed so much that the undercooling is high enough for bainite formation, which occurs at the expense of $\alpha_W$. Thus $\alpha_W$ will not form as a distinguishable phase ($W_s\neq B_s$). Again elements such as Mo, which for unexplained reasons, remove grain boundary nucleation sites will reduce the amount of $\alpha_W$ form in a similar way to allotriomorphic ferrite ($\alpha_a$).

Boron, which has a strong retarding effect upon the nucleation of allotriomorphic ferrite ($\alpha_a$) has a negligible effect upon displacive transformation products and would not be expected to retard formation of $\alpha_W$. Widmanstätten ferrite is an undesirable constituent because of its inferior toughness properties\[^{16,17}\].

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* If a plate or lath is idealised as a rectangular parallelepiped with sides of lengths $a$, $b$, and $c$, then $a\approx b\approx c$ for a plate and $a\approx b\approx c$ for a lath.
Fig. 1.2: The back-to-back growth of Widmanstätten ferrite plates in order to mutually accommodate their shear displacements.

Fig. 1.3: Multidirectional diffusion in case of Widmanstätten ferrite as compared with diffusion just ahead of the interface in case of allotriomorphic ferrite growth.
1.3.9 The Bainite Transformation

Bainite, another product of a displacive reaction, is a non-lamellar aggregate of plate-shaped ferrite and carbides. However, in some cases carbides may be totally absent\[^{[18]}\] *e.g.*, upper bainite in Si steels. The bainite transformation has been summarised by Christian and Edmonds\[^{[19]}\] and more recently by Bhadeshia and Christian\[^{[20]}\]. It is concluded that the incoherent ledge mechanism of growth, as proposed by Aaronson *et al.*\[^{[21]}\], is not probable for bainite. Furthermore, it is now established that the transformation can only occur at a certain degree of undercooling below the $T_0$ temperature\(^*\). The undercooling required is lower than that associated with the athermal martensite transformation, primarily due to the lower stored energy of bainite, and because of specific differences in nucleation behaviour, *i.e.*., the nucleation of bainite does involve the partitioning of carbon\[^{[22]}\] whereas for martensite both nucleation and growth are diffusionless.

---

Fig. 1.4: The morphology of bainite as it nucleates at prior austenite grain boundaries, and then autocatalytic nucleation of sub-units result in the formation of a sheaf. It should be noted that sub-units are continuous.

\(^*\) **The $T_0$ temperature refers to a temperature at which ferrite ($\alpha$) and austenite ($\gamma$) of identical composition have the same free energy.**
Bainite grows by a diffusionless mechanism, but because of the relatively high temperatures at which it occurs, the excess carbon is either rapidly rejected into the remaining austenite or precipitates in the form of carbides in the ferrite. The relatively low driving force at the $B_s$ temperature leads to a limited sub-unit size, (Fig. 1.4) the limitation coming into force when the chemical free energy change can no longer drive the transformation interface through the myriad of accommodation defects that are found to accompany the formation of bainite. The isothermal character of bainite transformation arises since new subunits can only nucleate autocatalytically when the carbon concentration in the vicinity of the prior subunit (i.e., the carbon build-up resulting from post-bainitic partitioning) is reduced by diffusion to a sufficiently low level such that displacive transformation is thermodynamically allowed. At a certain degree of transformation (depending on temperature and alloy composition), the carbon content of the austenite will reach a level such that the $T_0$ condition is transgressed, and displacive transformation then ceases. This is the incomplete reaction phenomenon, the term incomplete referring to the fact that the reaction stops well before the carbon content of the austenite reaches the level specified by the $\alpha + \gamma/\gamma$ equilibrium or paraequilibrium phase boundaries. Direct observations (at atomic resolution) have shown\textsuperscript{[23]} that segregation induced solute drag cannot be claimed to influence the growth of bainite. The bainite bay in alloy steels is probably due to the overlapping of separate C-curves for the different reactions rather than to solute drag on a ferrite-austenite interface. The observed shape change implies an atomic correspondence during growth, the necessity for which arises from the low mobility of the iron atoms at the transformation temperatures.

There are two classical morphologies of bainite.

1.3.3.1 Upper Bainite

This consists of platelets of ferrite adjacent to each other, and in very nearly the same crystallographic orientation in space, so that wherever two adjacent platelets touch, a low angle boundary arises. Elongated cementite particles usually decorate the boundaries of these platelets, the amount and continuity of these slabs of cementite depending on the carbon content of the steel. The ferrite platelets, which form a sheaf, have the same habit plane, and the sheaf itself has a thin wedge plate morphology in three dimensions. The slabs of cementite actually form from the austenite between the
ferrite platelets, and hence do not have a reproducible orientation relation with the \( \alpha \) since they precipitate from austenite. Fig. 1.5 illustrates schematically the transition from upper bainite to lower bainite.

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**Fig. 1.5:** When the time to decarburise the ferrite is small relative to that required to relieve the carbon supersaturation by the precipitation of carbides within the ferrite, then upper bainite is obtained; otherwise, lower bainite forms\(^{[24]}\).

### 1.3.3.2 Lower Bainite

This is basically very similar to upper bainite, except that the amount of interplate cementite is less, and carbides can be found within the ferrite itself. These intra-ferrite carbides can be epsilon carbide (in high-carbon or medium carbon silicon steels) or cementite plates precipitated in a single crystallographic orientation with respect to \( \alpha \), with the habit plane inclined at about 60° to the plate axis. There are however cases where more than one variant can be observed\(^{[25,26]}\).

The orientation relationship between bainitic ferrite and austenite is close to either the Kurdjumov-Sachs or the Nishiyama-Wasserman orientation. The ferrite and cementite are relatively oriented by a variant of the Bagaryatskii relationship commonly observed for the precipitation of cementite in tempered martensite, or other kinds of tempering orientation relationships.
1.9.4 Acicular Ferrite

Acicular ferrite appears as a fine grained interlocking array of non-parallel laths. Recent work\cite{27,28} has shown that acicular ferrite is in fact intragranularly nucleated bainite. It differs morphologically from classical sheaf-like bainite firstly because it nucleates intragranularly, either on inclusions, or sympathetically on pre-existing plates, secondly because growth is limited by physical impingement with other plates which form on neighbouring sites. This is shown schematically in Fig. 1.6. Acicular ferrite requires the presence of inclusions to enable intragranular nucleation and will only form when the austenite grain size is relatively large, so that events originated from the grain boundaries do not swamp those occurring intragranularly. Intragranular nucleation on inclusions has a higher activation energy when compared with grain boundary nucleation\cite{29} so that the number of grain boundary nucleation sites must be minimised to obtain acicular ferrite.

![Diagram of acicular ferrite](image)

**Fig. 1.6:** Randomly placed acicular ferrite nucleates on the inclusions and is just another variant of bainite which nucleates at prior austenite grain boundaries and exhibits aligned morphology.

Acicular ferrite is a highly desirable constituent in steel welds due to its fine grain size and interlocking nature, often referred to "basket weave structure"\cite{30}. The large number of non-parallel grain boundaries hinder crack propagation and the impact toughness is thus improved\cite{31-33}.
1.3.5 Martensitic Transformation

Martensitic transformations are a subclass of displacive, diffusionless, and first-order phase transformations in which the kinetics and morphology are dominated by the strain energy arising from shear-like displacements. The transformation kinetics are controlled by the nucleation rate and not by the growth rate because the growth rate is relatively fast. A necessary condition for the occurrence of martensitic transformation is that the free energy of martensite should be lower than that of austenite. Moreover, since additional energy, such as that due to surface energy and transformation strain energy, is necessary for the transformation to take place, the difference between the free energies of austenite and martensite must exceed the required additional energy. Therefore the austenite to martensite transformation cannot occur until the specimen is cooled to a particular temperature below the value where the free energy difference between austenite and martensite is zero. This temperature is called martensitic transformation start temperature \( (M_s) \). The overall kinetics of martensitic reactions is greatly influenced by autocatalytic nucleation\(^{[34]}\), but the phenomena have received relatively little systematic study so far. Martensitic transformation kinetics in steels are either athermal or isothermal.

1.3.5.1 Autocatalytic Nucleation

The preexisting sites are not enough to account for all the martensitic units observed. These excess sites are generally attributed to autocatalysis. Three mechanisms\(^{[35]}\) have been proposed for autocatalysis, relying on the fact that immediate vicinity of a plate is disturbed quite severely by a combination of elastic and plastic deformation processes due to the shear like nature of the transformation.

- **Stress-induced Nucleation, i.e.,** the activation of less potent defects at a given temperature by the internally generated elastic stresses.
- **Strain-induced Nucleation, i.e.,** the creation of new and more potent nucleating defects by the dislocation generation and rearrangement during plastic accommodation of the parent phase in response to the transformational shape change.
- **Interfacial Autocatalysis, i.e.,** direct nucleation of new martensitic units from the existing martensitic interfacial dislocations by a secondary dissociation process.
1.4 Role Of Alloying Elements in Transformation Kinetics Steels

The aim of this section is to mention briefly how alloy additions influence transformations in steels. Specific effects are dealt with in detail as they arise in the text. The effect of alloy elements in steels is twofold. They can affect both the thermodynamics and kinetics of transformations. The hardenability of steels is related directly to the influence on the nucleation and growth kinetics of the decomposition products. Primarily, hardenability of steels is defined in terms of the mean depth and distribution of martensite in specimens quenched under standard conditions. The ability to form martensite is dependent, in turn, on the ability to suppress (partially or completely) the formation of other austenite decomposition products such as allotriomorphic ferrite and cementite, pearlite, and bainite. For a given steel, a useful index of the ability to suppress the reconstructive transformation of austenite is the location of the nose (or noses) on the corresponding time-temperature-transformation (TTT) curve. Recognising that this location is determined by the nucleation and growth kinetics of the decomposition products, it is important to consider the influence of alloying elements on the kinetics of reaction.

The effect of alloying elements on the transformation of austenite has been studied considering the behaviour of an alloying element in and close to the moving interface. The rate at which an interface moves depends both on its intrinsic mobility (\textit{i.e.}, related to the process of atom transfer across the interface) and on the ease with which any alloying element partitioned during transformation diffuses ahead of the interface. Both of these processes dissipate the free energy ($\Delta G$) available for interface motion; when $\Delta G$ is mainly used up in driving the diffusion of solute ahead of the interface, growth is said to be diffusion-controlled. On the other hand, interface-controlled growth occurs when most of $\Delta G$ is dissipated in the process of atom transfer across the interface. In Fe-X-C ternary systems (where X is a substitutional alloying element), the diffusion-controlled growth is complicated by the fact that both interstitial and substitutional atomic diffusion occurs during transformation. Substantial differences in the diffusion coefficients of the interstitial and substitutional elements along with the assumption of local equilibrium at the interface leads to a variety of possible growth modes.
1.4.1 Partitioning Local Equilibrium (P-LE)

For low supersaturations, X (the substitutional solute) partitions between the daughter (α) and parent (γ) phases. The flux of C is reduced by making the C-concentration gradient very shallow (Fig. 1.7a). The precipitate growth rate is low and is determined by the slow diffuser X i.e., X exerts a diffusional drag on the growth kinetics, which is consequence of the fact that it diffuses many orders of magnitude slower than carbon.

1.4.2 Negligible Partitioning Local Equilibrium (NP-LE)

For rather high supersaturations, the precipitate growth rate is relatively high and is determined by the fast diffuser, C. In this regime, X, exerts essentially no diffusional drag effect, in spite of its low diffusivity. The gradient of X is made very steep to increase flux (Fig. 1.7b), by partitioning very little X from γ to α. As supersaturation is changed by alloying element additions, both nucleation and growth should be influenced in the same way, i.e., accelerated for increased supersaturations, and retarded for decreased supersaturations.

A given bulk composition is expected to pass from NP-LE to P-LE regime with increasing temperature. During NP-LE growth the width of the X concentration spike in γ can be a few nm. As the temperature of transformation decreases, the X concentration spike also decreases until it becomes approximately equal to atomic dimensions. It is usually assumed that the condition is then reached where the substitutional atoms become configurationally frozen, and equilibrium breaks down at interface. This constrained equilibrium, in which X is not redistributed during transformations, is known\[42\] as “paraequilibrium”. However, C is still mobile, and subject to the constraint that Fe/X ratio is identical in α and γ, it reaches “equilibrium”. It is currently not possible to decide theoretically which of these modes is favoured in a particular set of circumstances, and experimental evidence does not help since it is not in general sufficiently precise. The possible existence of solute drag effects and interface pinning effects may further complicate the interpretation of experimental evidence. All these effects are expected to be more complicated in the case of segregated steels.
Fig. 1.7: If local equilibrium is maintained at the $\alpha/\gamma$ interface, two modes of allotriomorphic ferrite growth in Fe-C-X (where $X$ is a substitutional alloying element) are possible, depending on the alloy composition. These modes are shown in the above diagrams, where $X$ is Mn (after Bhadeshia\cite{15}). (a) Growth at low supersaturations (P-LE) with bulk redistribution of Mn, (b) growth at high supersaturations (NP-LE) with negligible partitioning of Mn during transformation.
1.5 Prediction of Microstructure

Bhadeshia et al. [43–47] have developed a model to predict the microstructure in low alloy welds using the phase transformation theory outlined in the previous sections and can be applied to wrought steels. The steps involved in the calculations of microstructure in this model are represented in a flow chart (Fig. 1.8).

Fig. 1.8: Flow chart illustrating the steps involved in the calculation of the microstructure. $T_h$ is the high temperature at which allotriomorphic ferrite ($V_a$ in the diagram) starts forming. $q$ is the half thickness of allotriomorphic ferrite layer $T_l$ is the temperature below which displacive transformations are assumed to be kinetically favoured and is obtained by the cross-over point of the two C curves. $t_1$ is the time taken for the weld deposit to cool from $T_h$ temperature to $T_l$ temperature. $t_3$ is the time available for Widmanstätten ferrite to grow right across the austenite grains. $t_c$ is the critical time before an impingement occurs (after Bhadeshia et al. [48]).

To start with austenite grains are assumed to have a morphology of hexagonal prisms as illustrated in Fig. 1.9. An estimation of solute segregation during solidification (assumed to be equilibrium) is made on the basis of their segregation tendencies. From the knowledge of chemical composition, austenite grain size parameters and
cooling curve, phase diagrams and time-temperature-transformation (TTT) curves are calculated for solute-enriched and solute-depleted regions. The model assumes all the alloying elements to be in solid solution and is valid for up to 5 wt.% of total alloying additions.

Fig. 1.9: For the purpose of modelling the austenite grains are approximated as space filling hexagonal prisms.

1.5.1 Isothermal Transformation Diagrams

Bhadeshia's empirical model to generate the time-temperature-transformation (TTT) diagrams for the alloy steels, containing C, Mn, Si, Ni, Cr, Mo and V is formally based on Russell's equation\[49\] for incubation time:\*

\[ \tau_s \propto \frac{T}{(\Delta G_m^p)^p D} \] (1.1)

where

\( \tau_s = \) time taken to establish a steady-state nucleation rate,

\* The incubation time is in the actual analysis taken to be the time period before the onset of a detectable amount of isothermal transformation and this does not really correspond to \( \tau_s \) as defined in Russell's equation.
\begin{align*}
T &= \text{absolute temperature}, \\
D &= \text{appropriate diffusion coefficient related to boundary or volume diffusion, depending on the coherency state of the nucleus concerned}, \\
p &= \text{an exponent, depending on the nature of the nucleus}, \\
\Delta G_m^v &= \text{the maximum volume free energy change accompanying the formation of a nucleus in a large amount of matrix phase.}
\end{align*}

Referring to equation 1.1, and using the theory of diffusion coefficients\cite{50}, Bhadeshia obtained

\begin{equation}
D \propto \exp \left( \frac{S}{R} \right) \exp \left( -\frac{Q}{RT} \right) \tag{1.2}
\end{equation}

where \( S \) is the activation entropy for diffusion and \( Q \) is the activation enthalpy for diffusion. Substituting this result in equation 1.1, assuming \( \tau = \tau_s \), and multiplying \( \Delta G_m^v \) by the molar volume of ferrite, following relation was obtained

\begin{equation}
\ln \left[ (\Delta G_m)^p \frac{T}{T} \right] = \frac{Q}{RT} + C_1 \tag{1.3}
\end{equation}

where \( \Delta G_m \) is the chemical free energy change accompanying the formation of 1 mol of nucleating system in a large amount of matrix phase and \( C_1 \) is a constant.

1.5.1.1 Calculation of Chemical Free Energy Change for Nucleation

Fig. 1.10 shows Gibbs free energy curves for austenite and ferrite as a function of their carbon concentrations. Let the carbon content of the alloy be \( \bar{x} \) and the free energy of \( \gamma \) of composition \( \bar{x} \) is represented by the point \( \bar{G} \). The free energy of the specimen can be lowered as far as the point \( p \), by the formation of a mixture of \( \gamma \) of composition \( x_\gamma^\gamma \) and \( \alpha \) phase of composition \( x_\alpha^\alpha \). The precipitation process is initially very slow as the nucleation barrier must be overcome\cite{51}. Because of the negligible volume of any nucleus, it may be assumed that its formation leaves the parent phase unchanged with respect to composition. Then, the formation of a nucleus with the composition \( x_m \) should involve transfer of the mole fraction \( x_m \) carbon atoms from a higher chemical potential state to a lower chemical potential state. From the geometry of the graph it can be seen that the free energy change is represented by the vertical distance \( \Delta G_m \) if the point \( m \) represents the free energy of the nucleus. Actually, the point \( m \) does not
represent the free energy of the nucleus (capillary effects are ignored as any dependence of surface energy on composition). From the diagram, it is apparent that the free energy change \( \Delta G_m \) for nucleation will be maximum for a nucleus of composition \( x_m \) and \( \Delta G_m \) can thus be calculated using the parallel tangent construction as illustrated.

The use of the nucleation composition corresponding to the maximum \( \Delta G_m \) is a very good approximation for steels, since the solubility of carbon in ferrite is so limited that any carbon concentration up to the equilibrium level makes small difference to the magnitude of \( \Delta G_m \). Numerical value of \( \Delta G_m \) can be obtained from the following equation\(^\text{[52]}\) deduced from Fig. 1.10

\[
\Delta G_m = RT \ln \left( \frac{a^\alpha_C(x_m)}{a^\alpha_C(x)} \right) \tag{1.4}
\]

where \( a^\alpha_C(x_m) \) denotes the activity of carbon in the ferrite of composition \( x_m \) and \( a^\alpha_C(x) \) denotes the activity of carbon in austenite of composition \( x \). The ideal nucleus composition, \( x_m \), is determined by iterative solution of the equation\(^\text{[52]}\)

\[
\Delta G^{\gamma\rightarrow\alpha}_{Fe} + RT \ln \left( \frac{a^\alpha_Fe(1-x)}{a^\gamma_Fe(1-x)} \right) - RT \ln \left( \frac{a^\alpha_C(x)}{a^\gamma_C(x)} \right) = 0 \tag{1.5}
\]

where \( \Delta G^{\gamma\rightarrow\alpha}_{Fe} \) is the free energy change accompanying the austenite to ferrite transformation in pure iron and \( R \) is the gas constant. \( a^\alpha_Fe(1-x) \) denotes the activity of iron in ferrite of composition \( (1-x) \) and other activity terms can be defined likewise. The values of \( p \) and \( D \) are fixed by a curve fitting to experimental data and \( \tau \), is assumed equal to \( \tau \) (the incubation time). Therefore, this method precludes any preconceived ideas regarding the shape, the coherency or the size of the initial nucleus. The method is capable of reproducing the critical bay region of the time-temperature-transformation (TTT) curves. The calculations generate two 'C' curves as function of time and temperature, one representing the reconstructive transformation and the other representing the displacive reactions (Widmanstätten ferrite, acicular ferrite and bainite) as illustrated in Fig. 1.11. It is also possible to predict relative shifts in these component curves, as a function of alloying element content. In the case of lower 'C' curve the diagram is truncated at the \( W_s \) (or \( B_s \) when Widmanstätten ferrite formation is not possible), since this represents an upper limit for the Widmanstätten ferrite and bainite reactions.

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Fig. 1.10: Parallel tangent construction to find maximum free energy for the nucleation of ferrite.

Fig. 1.11: A schematic time-temperature-transformation (TTT) diagram showing two distinct 'C' curves.
The analysis does not consider austenite grain size variations, but it has been pointed out\[53\] that such variations are relatively small at least as far as the onset of transformation is concerned. The calculations of Widmanstätten ferrite, bainite and martensite start temperatures are illustrated in Fig. 1.12. Both bainite and Widmanstätten ferrite nuclei are assumed to have the carbon concentration consistent with the maximum free energy change, although during growth the bainitic ferrite may become supersaturated with carbon. The temperature at which displacive products can be formed is decided by $\Delta G_N$, which is defined as the minimum free energy needed for the austenite to transform displacively to ferrite.

Fig. 1.12: Schematic representation of calculation of $W_s$, $B_s$, $M_s$ temperatures for low (A), medium (B) and high alloy (C) compositions\[22\]. It should be noted that $G_1=50$ J/mol and $G_2=400$ J/mol are the stored energies of $\alpha_W$ and $\alpha_b$ respectively. $\Delta G_\gamma^\gamma-\alpha$ is the free energy change accompanying the formation of $\alpha$ of the same composition as $\gamma$. While $\Delta G_\gamma^\gamma-\gamma'+\alpha$ is the free energy change accompanying the formation of ferrite which at all times contains an equilibrium carbon content. For alloy steels this term is computed on the basis of no substitutional element partitioning.
1.5.2 Phase Diagrams

The construction of the phase diagrams involves calculations of the phase boundary lines derived from the available free energy for transformation and is illustrated in Fig. 1.13. The calculations in the model are based on Lacher, Fowler and Guggenheim model\cite{54}. Ferrite growth without a change in composition can only occur below the \( T_0 \) temperature at which stress free \( \alpha \) and \( \gamma \) of identical composition have equal free energy\cite{15}. The \( T_0 \) temperature lies between the \( A_{e3} \) and \( A_{e1} \) temperatures which in turn define the upper and lower limits of the two phase \( \alpha + \gamma \) field. Bainite (\( \alpha_b \)) and Widmanstätten ferrite (\( \alpha_W \)), both grow by a displacive transformation mechanism. The formation of \( \alpha_W \) involves the redistribution of carbon between the parent and product phase, but \( \alpha_b \) initially forms by a diffusionless mechanism and the carbon later partitions into the remaining austenite. In the transformation of bainite, the whole of the austenite does not transform instantaneously. The transformation starts from the austenite grain boundaries; even though the initial plate forms without diffusion, it has an opportunity to reject its excess carbon into the residual austenite. Any further increment of transformation is, therefore, associated with a lower free energy change, due to the higher carbon content of the austenite from which it has to form. Eventually, a stage is reached when the transformation becomes thermodynamically impossible since the free energies of the residual austenite and bainite become identical\cite{15,22,52,55}. The locus of such positions, as a function of isothermal transformation temperature defines the \( T_0' \) curve\footnote{The \( T_0' \) curve is the \( T_0 \) curve modified to take account of the strain energy accompanying the Invariant Plane Strain (IPS) shape change during transformation. Invariant Plane Strain may be regarded as a simple shear on the invariant-plane, together with an expansion or contraction normal to this plane\cite{57}.} (Fig. 1.13), where \( \gamma \) and \( \alpha_b \) (with a certain amount of stored energy associated with transformation strains) of the same composition have equal free energies.

The bainite reaction should therefore stop when the carbon concentration of the austenite reaches the level given by the \( T_0' \) for the isothermal transformation temperature concerned. The \( A_{e3}' \) curve may be similarly defined for the growth of \( \alpha_W \), which involves the paraequilibrium transformation with the partitioning of carbon, (but not of substitutional alloying elements). For plain carbon steels, it follows that the \( A_{e3}' \) and
Fig. 1.13: Schematic diagram showing the construction of phase boundaries from free energy data. The $T_0$ line includes the effect of 400 J/mol of strain energy due to transformation (after Yang and Bhadeshia\cite{56}).

$A_{e3}$ curves are identical. The aim of this project is to predict development of microstructure in chemically heterogeneous alloys using the above model as a basis.
REFERENCES


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Chapter 2

HETEROGENEITY AND PHASE TRANSFORMATIONS

2.1 Introduction

Most industrial alloys usually have some degree of chemical heterogeneity, because they undergo thermo-mechanical treatments which are generally inconsistent with the achievement of thermodynamic equilibrium. Chemical segregation can have a profound influence on allotropic transformations and consequently on microstructure and properties, especially when the general level of alloying additions is large. This work is an attempt to understand quantitatively the manner in which composition fluctuations, of the kind encountered in industrial practice, influence both the nucleation and growth characteristics of solid-state phase transformations, and ultimately to relate the work to the influence of segregation on mechanical properties.

2.2 Chemical Heterogeneity

Segregation, which results in compositional heterogeneity in cast steels, is primarily an effect of non-equilibrium primary crystallization from the melt. The degree of heterogeneity depends on the amount and nature of the alloying elements and impurities present, and the cooling conditions. In general, the wider the crystallization temperature range, or more precisely, the greater the range of equilibrium concentrations represented during crystallization between the liquid and solid phases, the greater the segregation. Segregation is generally classified as:

- (a) microsegregation, which extends over distances of the grain diameter or less and
- (b) macrosegregation, which can extend over many grain diameters.

2.2.1 Solute Redistribution

Consider the solidification of an alloy of mean composition $X_0$ in the binary system as shown in Fig. 2.1. According to solidification theory, any of the following three limiting cases may govern the transformation:\[1\]:

- Solidification occurs under complete equilibrium conditions.
- Solidification is not an equilibrium process and no diffusion occurs in the solid, but perfect mixing occurs in the liquid.
Solidification is not an equilibrium process, no diffusion occurs in the solid, and the mixing in the liquid is not perfect but occurs by diffusional processes only.

In practice, solidification does not occur under equilibrium conditions, so the first point can be neglected. To begin with, the assumption that the negligible diffusion in the solid phase is a good first approximation to make. In the initial stages of solidification good mixing of the liquid seems likely due to turbulence in the melt.

Fig. 2.1: The non-equilibrium solidification of an alloy, $X_0$, in a binary system.[1]

Consider the unidirectional solidification of a volume element of an alloy of composition $X_0$ (Fig. 2.1) which has a liquidus temperature $T_1$. The first solid to form contains $kX_0$ of solute and it will be purer than the liquid from which it forms, as $kX_0 < X_0$, where $k$ is the partition coefficient*. Due to the solute enrichment of the liquid, it's new liquidus temperature will be lower than $T_1$. As this sequence of events continues the liquid becomes progressively richer in solute and solidification occurs at progressively lower temperatures. Since, initially, there is perfect mixing of the melt, for a given temperature the compositions of the solid and liquid in contact with one another are given by the equilibrium phase diagram (Fig. 2.1). However, as there is no diffusion in the solid the separate layers of solid retain their original composition so that

* The partition coefficient ($k$) of an element is the ratio of the equilibrium concentration of the element in the solid to its equilibrium concentration in the liquid phase, i.e., $k = \frac{X_s}{X_L}$.
the mean composition of the solid is continuously lower than the solidus composition
given by the phase diagram. The true solidus is defined by \( X_s \) in Fig. 2.1. On the other
hand, the liquid becomes progressively richer in solute and may even attain eutectic
composition at the temperature \( T_E \). The corresponding composition profile will thus
progress as shown in Fig. 2.2. The completely solidified volume element will then have
a solute distribution as shown in Fig. 2.2c with \( \bar{X}_s = X_0 \) The variation of \( X_s \) along
the solidified volume element can be obtained\(^2\) by equating the solute rejected into
the liquid when a small amount of solid forms with the resulting increase of solute in
the liquid. Ignoring the difference in molar volumes between the solid and liquid this
gives:

\[
(X_L - X_s)df_s = (1 - f_s)dX_L
\]

where, \( f_s \) is the volume fraction solidified.

Integrating this equation using the boundary condition \( X_s = kX_0 \) at \( f_s = 0 \) gives\(^2\)

\[
X_s = kX_0(1 - f_s)^{(k-1)}
\]

and

\[
X_L = X_0 f_L^{(k-1)}
\]

\( X_s \) and \( X_L \) are the mole fraction of solute in the solid and liquid in equilibrium at a
given temperature.

Equations 2.2 and 2.3 are known as the non-equilibrium lever rule or the Scheil’s
equations. It should be noted that for \( k < 1 \), these equations predict that when
there is no diffusion in the solid there will always be some eutectic in the last drop
liquid to solidify, no matter how little solute is present. However, as the solidification
goes to completion it seems likely that convectional mixing gives way to diffusional
mixing. Thus, there will be a build-up of solute ahead of the growing crystal, with a
correspondingly rapid increase in alloying content of the solid that forms as shown in
Fig. 2.3a. If solidification is made to occur at a constant rate, \( v \), it can be shown that a
steady state is finally obtained when the interface temperature reaches \( T_3 \) in Fig. 2.1.
**Fig. 2.2:** The composition profile in a solidifying cylindrical bar under conditions of perfect mixing in the liquid and no diffusion in the solid\textsuperscript{[1]}.

**Fig. 2.3:** The composition profile of a solidifying bar under conditions of no diffusion in solid but with diffusional mixing in liquid\textsuperscript{[1]}. 
During steady-state growth the concentration profile in the liquid must be such that the rate at which solute diffuses down the concentration gradient away from the interface is balanced by the rate at which solute is rejected from the solidifying liquid, \( i.e., \)

\[
\frac{-dX_L}{dx} D = R'(X_L - X_s) \quad (2.4)
\]

where \( D \) is the diffusivity of the solute in the melt, \( \frac{dX_L}{dx} \) refers to the concentration gradient into the liquid and \( R' \) is the growth speed of the crystal. If the diffusion equation is solved for steady-state solidification it can be shown that the concentration profile in the liquid ahead of the interface is given by the following equation

\[
X_L = X_0 \left[ 1 - \frac{1 - k}{k} \exp \left( \frac{-xR'}{D} \right) \right] \quad (2.5)
\]

This equation indicates that \( X_L \) decreases exponentially from \( \frac{X_0}{k} \) at \( x = 0 \) (i.e., the interface) to \( X_0 \) at some large distance from the interface. \( \frac{D}{R'} \) gives the characteristic width of the concentration profile. In the final stages of solidification, the ‘bow-wave’ of solute is compressed into a comparatively small volume of liquid and the solute concentration is thus expected to rise rapidly as in Fig. 2.3c. In terms of weld solidification, this suggests that the last stages of weld solidification are associated with the highest level of segregation. Miller\(^3\) has established the presence of a solute-rich layer ahead of the advancing solid/liquid interface in a weld pool and, using microprobe analysis on back-filled weld metal cracks, has also shown that the values of the equilibrium distribution coefficients for a variety of solute elements are the same in both weld-pool solidification and ingot solidification. The basic mechanism of solute segregation thus appears to be the same in both cases and, just as in ingot solidification, microsegregation is more pronounced in a weld bead, the more dendritic is the solidification mode.
2.2.2 Segregation

Segregation is classified as either microsegregation (extending over distances of the grain diameter or less) or macrosegregation (extending over more than several grain diameters). In turn microsegregation is subdivided into cellular, dendritic and grain boundary segregation. In the welds, at the side of the pool steep thermal gradients together with comparatively low solidification rates favour cellular growth while at the weld centre line, high solidification rates promote a transition to dendritic growth modes. The detailed nature of the segregation pattern is dependent on the growth conditions and morphology of the growing dendrites and is largely a manifestation of liquid flow in the semi-solid region\textsuperscript{[4-8]}.

The segregation behaviour of a steel depends largely on whether ferrite or austenite forms during non-equilibrium solidification. An alloy has the lowest free energy when it is in a homogeneous condition, and this is the driving force for diffusion. There is a large difference in the rate of diffusion of alloying elements in these two phases. Because γ-iron has a close-packed crystal structure whereas α-iron is more loosely-packed. The latter allows easier passage through the structure of vacancies and associated solute atoms. As a general rule, it may be stated that the diffusion coefficient doubles for every 20 °C rise in temperature. Table 2.1 shows typical diffusion coefficients of different alloying elements in α and γ at 700 °C.

\[D_\alpha \text{ and } D_\gamma \text{ are the diffusion coefficients in } \alpha \text{ and } \gamma \text{ respectively.} \]

In contrast to carbon, the diffusion rate in austenite for substitutionally dissolved elements is very low and only a small amount of alloying elements can pass through austenite from the liquid into the ferrite.

Numerical calculations for austenite show that so-called back diffusion\textsuperscript{*} is important only towards the end of the solidification, and hardly effects the central parts of the dendrite arms. Calculations for ferrite indicate that back diffusion is very significant, and a dendrite arm can have an almost uniform composition just behind the solidification front.

\textsuperscript{*} Back diffusion is the diffusion of alloying elements from the liquid to the solid due to concentration gradient established between the two during solidification.
Table 2.1: Diffusion coefficients$^{[9-11]}$ of different alloying elements in $\alpha$ and $\gamma$. However it should be noted that the data represent a simplification as these coefficients are concentration dependent.

Using an approximate method Brody and Flemings$^{[12]}$, derived an equation to take account of back diffusion.

$$X_t = X_0 \left[ \frac{1 - f}{1 + A} \right]^{-(1-k)}\tag{2.6}$$

Where $A$ is a parameter defined as follows:

$$A = \frac{kD^*\theta}{\lambda^2}$$

where

$D^*$=diffusion constant in solid state,

$\theta$=the total solidification time,

$\lambda$=half of the dendrite arm spacing, and

$X_0$=composition of the alloy.

The "A" term depends on the back diffusion and is a correction term to the original Scheils' equations.
The equation shows that, as long as the ‘A’ term is much less than \((1 - f)\), the distribution can be fairly well described by the original Scheil’s segregation equation. As \((1 - f)\) grows smaller towards the end of the solidification process, the importance of back diffusion increases. This is an effect of the very steep concentration gradient at the end of the solidification process. Segregation is also influenced by differences in the partition coefficients between ferrite and liquid, or austenite and liquid, for different alloying elements; the cooling rate will also have a major effect. The nature of the liquid \(\rightarrow\) solid transformation can itself have an important effect; in steels, primary solidification phase may be \(\delta\)-ferrite or austenite. The intensity of segregation is expressed in a convenient, quantitative manner by the segregation ratio \(S_i^i\) for an alloying element “i”. It is defined as the ratio between the highest and lowest values of the concentration in a dendrite. This quantity can be calculated by applying equation 2.6 at \(f = 0\) and \(f = 1\), assuming that \(X_{\delta} = kX_{\gamma}\) in both cases.

\[
S = \left(\frac{1 + A}{A}\right)^{1-k}
\]  

(2.7)

The segregation ratio increases with increasing cooling rate and with decreasing partition coefficient\[^13\]. Table 2.2 shows the calculated partition coefficients between \(\delta\)-iron and liquid \((k_{\delta/l})\) and between austenite and liquid \((k_{\gamma/l})\). Flemings\[^{14}\] has tabulated experimental results for microsegregation in some iron based alloys; these values are shown in Table 2.3, where \(S_i\) varies from 1.0 to over 4.0.

Among the metals, Mn should produce extensive segregation on a dendritic scale\[^{16}\]. This is due to the fact that the addition of Mn to Fe-C alloys extends the \(\gamma\) phase region in the Fe-C diagram as shown in the Fig. 2.4.

Alloys with higher C and Mn contents can solidify directly to austenite\[^{17}\]. If that happens, the heterogeneity of the \(\gamma\)-solution is considerably higher than for the case of primary \(\delta\) solidification, since there is a greater range of equilibrium concentrations represented during the direct solidification of the melt to \(\gamma\)-solution, and because the solid state diffusion of substitutional elements is more sluggish in austenite so that homogenisation during cooling is also more sluggish. Cu, Sn, Mo, W, V, and probably Co also exhibit appreciable segregation. Nickel produces a fairly small dendritic segregation, Cr and Si generally produce only slight dendritic segregation.
Table. 2.2: Partition coefficients calculated, to a first approximation, by the expression \[ k_i = e^{\frac{\Delta G_i^0}{RT}} \], of alloying element 'i'. \( \Delta G_i^0 \) is the Gibbs free energy change per mole in transferring the pure element 'i' from the \( \delta \) to the liquid state and 'R' is the universal gas constant.

<table>
<thead>
<tr>
<th>ALLOYING ELEMENT</th>
<th>( k_i^{\alpha} )</th>
<th>( k_i^{\beta} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>0.06</td>
<td>0.29</td>
</tr>
<tr>
<td>Mn</td>
<td>0.76</td>
<td>0.81</td>
</tr>
<tr>
<td>Si</td>
<td>0.69</td>
<td>0.65</td>
</tr>
<tr>
<td>Ni</td>
<td>0.45</td>
<td>0.58</td>
</tr>
<tr>
<td>Cr</td>
<td>0.81</td>
<td>0.81</td>
</tr>
<tr>
<td>Mo</td>
<td>0.48</td>
<td>0.38</td>
</tr>
<tr>
<td>V</td>
<td>0.74</td>
<td>0.72</td>
</tr>
</tbody>
</table>

Table. 2.3: Experimental values of the segregation ratios (after Flemings\[^{14}\]).

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Alloying Element</th>
<th>Distance From The Chill (mm)</th>
<th>Segregation Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe-10Ni</td>
<td>Ni</td>
<td>12.5</td>
<td>1.35</td>
</tr>
<tr>
<td></td>
<td></td>
<td>50.0</td>
<td>1.38</td>
</tr>
<tr>
<td>Fe-26Ni</td>
<td>Ni</td>
<td>12.5</td>
<td>1.28</td>
</tr>
<tr>
<td></td>
<td></td>
<td>50.0</td>
<td>1.17</td>
</tr>
<tr>
<td>Fe-26Ni-33C</td>
<td>Ni</td>
<td>50.0</td>
<td>1.19</td>
</tr>
<tr>
<td>Fe-0.4C-1.8Ni</td>
<td>Mn</td>
<td>43.0</td>
<td>1.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>145.0</td>
<td>1.8</td>
</tr>
<tr>
<td>0.8Cr-0.7Mn</td>
<td>Ni</td>
<td>43.0</td>
<td>1.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>145.0</td>
<td>1.5</td>
</tr>
<tr>
<td>Fe-1.5Cr</td>
<td>Cr</td>
<td>12.5</td>
<td>1.0</td>
</tr>
<tr>
<td>Fe-1.5Cr-1.0C</td>
<td>Cr</td>
<td>12.5</td>
<td>4.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>50.0</td>
<td>4.1</td>
</tr>
</tbody>
</table>
Fig. 2.4: The addition of Mn to Fe-C alloys extends the $\gamma$-phase region in the diagrams for,

(a) a steel without Mn,
(b) a steel with 1.5 wt. % Mn,
(c) a steel with 2.5 wt. % Mn.
Among the non-metals, C, P, and S can be considered to have a marked ability to produce segregation, but the diffusion of one can be greatly affected by the presence of the others, as well as by other metal constituents. During solidification, the inclusions themselves are also subject to large and small scale spatial segregation. The silicate inclusions are concentrated in the arms of the dendrites, while the sulphur inclusions are usually located in the interdendritic spaces\textsuperscript{[18]}. An interesting observation has been the discovery of inclusion segregation\textsuperscript{[19]} in steel weld deposits, when the inclusions found at the cellular solidification boundaries.

Although the intensity of microsegregation is determined by the composition, the periodicity is controlled by the dendrite arm spacing. The dendrite arm spacing varies inversely with cooling rate to a power of between one-third and one-half\textsuperscript{[20]}.

2.2.3 Banding

For castings it has been proposed\textsuperscript{[21]} that solute-rich or solute-poor areas can result from fluctuations in the position of the growing liquid/solid interface. These fluctuations can be the result of periodic changes in heat flow and are analogous to those observed in arc welds when the arc energy is varying. Solute banding, which is a periodic enrichment and depletion of solute elements, is frequently observed in both manual and automatic welding, made with or without filler additions. When steel ingots are deformed the segregated areas are elongated into bands; a macroscopically laminated structure can therefore be caused by dendritic segregation. The banded structure proper which is found in worked materials under certain conditions has been investigated especially for annealed hypoeutectoid carbon steels. The reason seems to be that the alloys with this range of carbon content undergo direct melt to $\gamma$-solution transformation and experience a greater range of equilibrium concentrations during solidification, thus, resulting in greater segregation. Banding is favoured by austenitizing slightly above the $A_c_3$ point or, better still, between $A_c_3$ and $A_c_1$ temperatures. This is because the $A_c_3$ temperature is raised relative to the $A_c_1$ temperature under the influence of most segregated alloy elements (Fig. 2.5).
Fig. 2.5: Influence of alloying elements on the position of $\text{Ac}_1$ and $\text{Ac}_3$ temperatures (after Bastein, 1957).

(a) Influence of phosphorus.

(b) Influence of tin.
There has been general agreement for a number of years that the appearance of alternate pearlite and ferrite bands in rolled and forged hypoeutectoid steel products is primarily associated with persistent segregation of alloying elements other than carbon. This segregation originates in normal interdendritic segregation during solidification of the ingot, and because of the slow diffusion of many elements, particularly substitutional ones, at working and soaking temperatures, it persists in a more or less moderated form into the final product in a laminar distribution.

Jatczak et al. [22] regard the banding as being due to the opposing effects of solution elements and carbide formers on the location of carbon through their effect on the carbon activity in austenite at soaking temperatures, during cooling and during transformation. They found that carbide forming elements tend to increase carbon concentration in their vicinity, while solution type elements (e.g. Ni, Si, etc) tend to decrease carbon concentration in their vicinity. Therefore, in Fe-C-X type steels, the degree of carbon segregation and the location of high and low carbon areas relative to a fixed marker depends solely on the amount and distribution of the one alloying element, i.e., X. In multi-alloyed steels, these bands depend upon a balanced influence as determined by alloy types, amounts and distribution[22].

Bastien[18], on the other hand, emphasizes the role of the constitutional effect of the alloying elements in shifting the $\text{Ar}_3$ line, resulting in premature or delayed nucleation of proeutectoid ferrite. He suggests for example, in the case of P segregation, that since P-rich regions have a higher $\text{Ar}_3$ temperature the proeutectoid reaction will begin in these regions, rejecting carbon to P-depleted regions, and delaying the beginning of transformation there even further. However, in the case of P banding, the Jetczak[22] and Bastien[18] views are both tenable, since it is known that P increases the activity of carbon in austenite and will accordingly tend to repel carbon.

Kirkaldy et al. [23] examined quantitatively the banding behaviour in the ternary systems Fe-Si-C, Fe-Mn-C, Fe-Ni-C, Fe-Cr-C and Fe-P-C both as to the intensity of carbon segregation which occurs in the soaking (austenite) range and during the subsequent $\gamma$ to $\alpha$ transformation. The results confirm that the segregation of carbon which occurs before transformation is due to the equalization of the carbon activities. As

\* Activity is a thermodynamic function representing the change in the behaviour of a dissolved substance relative to the pure one.
expected from thermodynamic data, Si, Ni and P rich regions reject carbon, while Mn and Cr rich absorb it. They showed that the magnitude of carbon pre-segregation is in all cases only a fraction of the mean concentration, and does not increase significantly as the temperature is lowered towards the transformation temperature. Accordingly, the intense segregation which occurs in the room temperature microstructure of banded steels cannot be attributed to this phenomenon alone. However, this pre-segregation significantly influences the difference in $Ae_3$ temperature between adjacent layers and with it the sequence of ferrite nucleation across a segregated steel. Hence, pre-segregation affects the nucleation sequence by increasing the difference in nucleation temperature.

In evaluating the degree to which certain elements are responsible for banding, one must determine the extent to which each element is segregated during the initial solidification of the melt, and the rate at which the segregation will be reduced by diffusion. Qualitatively, we may assume that large partition coefficients and low diffusion coefficients will favour banding\textsuperscript{23}. Jatczak et al.\textsuperscript{22} found that isothermal treatment is more sensitive to the development of banded structures than is the case during continuous cooling but they did not go into any details of the transformations. Isothermal transformation results obtained by them are shown in the figure 2.6 for the Fe-0.42C-0.72Mn-0.29Si-0.82Cr-1.74Ni-0.25Mo wt. % steel.

Inclusions in steel which have been arranged into laminar through plastic deformation can, at least theoretically, play a part in the formation of the banded structure, either by favouring the physico-chemical reaction at the interfaces, or by locally modifying the chemical composition of the steel and thus altering it’s transformation points if they are slightly soluble in iron at a high temperature. According to Bastien\textsuperscript{18}, any theories which ascribe to the inclusions an essential role in the formation of banded structure are, however incorrect; for a given steel and for different cooling rates, inclusions of a particular type may sometimes be found in the ferrite and some times in the pearlite. Other reasons for rejecting such theories is the effect of a homogenization treatment at a high temperature which partly destroys the banded structure without affecting the inclusions.

\textsuperscript{*} Carbon pre-segregation refers to the segregation of carbon which occurs in the soaking range or before transformation.
2.3 Homogenization

It has been found out\cite{18} that the banded microstructure disappears when the cooling rate exceeds a certain value, which varies from one steel to another. Although the microstructural banding vanishes, but compositional banding does not. Hence, this disappearance of the banded microstructure is only temporary, and a further heat-treatment followed by slower cooling causes it to reappear. Small scale segregation can be removed by means of a long heat treatment at a high temperature in the austenite phase field, thus making the material chemically homogeneous. This is rarely the case in practice, mainly because of the low diffusion rates of most of the dissolved elements (except carbon) and also because of very low solubility of non-metallic inclusions in the solid state in iron. This segregation therefore persists, although to a more or less reduced extent, even after the high temperature heat treatments used for large forgings. Hence, the effectiveness of a homogenization treatment diminishes with increasing size of the forging, and especially near its centre\cite{18}.

Several investigations on this subject have shown that complete homogenization is very difficult to achieve and that in some cases it is necessary to raise the temper-
ature to 1300 which introduces other difficulties, such as overheating\(^*\) of the steel\(^{[24]}\). Certain workers\(^{[25]}\) have noted a relationship between the width of the bands and the temperature necessary to suppress them as shown in figure 2.7.

![Figure 2.7: Relationship between thickness of bands and reheating temperature (after Thompson and Willows\(^{[25]}\)).](image)

It is clear from figure 2.7 that there is a correspondence between the temperature required for the removal of the banded structure and the width of the bands. Since the homogenization time in a thermal treatment is proportional to the square of the dendrite arm spacing\(^{[26]}\), homogeneity is favoured by a short local solidification time. This time is defined as that between the initiation and completion of solidification at a given location in the ingot, and is inversely proportional to the average cooling rate at that location. Weinberg and Buhr\(^{[27]}\) reported that the distortion of the dendritic structure by hot working had little effect on the rate of homogenization of micro segregation in the AISI 4340 alloy steel composition. Inoculation with certain elements, *Overheating means heating a metal or alloy to such a high temperature that its properties are impaired. When the original properties cannot be restored by further heat treating, by mechanical working, or a combination of working and heat treating, the overheating is known as burning.*
e.g. calcium\(^{[28]}\), is sometimes employed to alter the ratio of dendrite arms to that of interdendritic spaces, although there is no change in the chemical composition of the dendrites.

Cox \textit{et al.} \[^{[29]}\] found that while heating sections of small laboratory-cast ingots of Fe-0.02C-0.25Mn-0.07Si-18.1Ni-5.85Mo-8.02Co-0.33Ti-0.005Al wt. % at 1232°C, the initial rate of homogenization is rapid, and may be sufficient to preclude the formation of reverted austenite during aging at 482°C. The rate later decreases to such an extent that complete homogenization by thermal treatment alone becomes impractical. Heating at 1200°C had a beneficial effect on the strength, ductility, and toughness of as cast maraging steel. Hot rolling of a 120mm thick ingot section to 15mm thick plate affected a reduction of microsegregation similar to that obtained by heating an ingot at 1200°C for 4 hours, but resulted in even greater increases in ductility and toughness. This may be due to the enhancement of diffusion during mechanical working which considerably accelerates homogenization\[^{[30]}\]. During plastic deformation, the movement and interactions of dislocations can result in the formation of vacancy defects. In so far as diffusion rate depends on vacancy concentration, mass flow will increase with high concentration of vacancies. The extent of this homogenization would be expected increase with increasing deformation, and should depend on the magnitude and distribution of the initial segregated solute.

2.4 Segregation and the Properties of Materials

Segregation affects the basic materials parameters such as interfacial energies, self-diffusivity and the morphology of the interfaces. The effect of banding on the mechanical properties of steels is usually considered to be detrimental, although, it is often the case that no marked improvement in properties can be obtained with less heterogeneous structures. According to Jatczak \textit{et al.} \[^{[22]}\], comparison of the longitudinal and transverse tensile properties of banded and of homogenized Fe-0.42C-0.72Mn-0.29Si-0.82Cr-1.74Ni-0.25Mo wt. % steel showed that only the transverse ductility was improved by homogenization, but even then the improvement was not commercially significant. Conversely, homogenization of through-the-thickness tension specimens of steel plate, (containing 1.47wt. % Mn, 0.21wt. %C) increased the strength by as much as 10% and the tensile ductility by at least a factor of 2.0, while the reduction in area was increased from 2.5 to 8.5 times by the homogenization\[^{[31]}\] (Fig. 2.8).
Fig. 2.8: Homogenized specimens showed improved strength and tensile ductility as compared to inhomogeneous (after Schwartzbart\[^{\text{31}}\]).

Wilms\[^{\text{32}}\] used commercial 50mm thick hot-rolled mild steel (Fe-0.22C-0.92Mn-0.07Si-0.012P-0.017S wt. %) to show that heterogeneity resulted in marked anisotropy, particularly with regard to impact properties and the tensile ductility. Similarly, Salmon Cox\[^{\text{29}}\], found that banding resulted in directional differences in plane-strain fracture toughness\(^*\). The highest fracture toughness was obtained when the crack plane and direction were oriented normal to the plane of banding, and the lowest occurred when both the crack plane and the crack direction were parallel to the plane of bands. In the former case it was noticed that the fracture frequently detoured abruptly from its main course when it encountered segregation bands normal to the crack plane and propagation direction. Thus, segregation bands appeared to act as small internal crack arrestors, which tended to impede and divert the main crack and forced it to follow

\[^*\] The plane-strain condition represents the more severe stress state in a crack opening mode when a tensile stress is applied in a direction normal to the faces of the crack. Plane-strain values of critical stress intensity factor are valid material properties, independent of specimen thickness, to describe the fracture toughness of strong materials. A stress intensity factor is a convenient way of describing the stress distribution around a flaw\[^{\text{33}}\].
a less direct path. This resulted in an increase in the measured fracture toughness of the material (Fe-0.013C-0.083Mn-0.069Si-18.1Ni-4.60Mo-7.71Co-0.47Ti-0.06Al wt. %) for this particular specimen orientation. However, it is important that the banding alone should not be considered when deciding the directionality of mechanical properties, since non-metallic inclusions have much greater effects. The inclusions not only act as regions of weakness but, depending on their shape relative to the test direction, can act as stress concentrators in the same way as a notch or crack. It has often been observed that notch ductility is lowest when the fracture runs parallel to the major axis of elongated inclusions[34]. It is important to recognize that satisfactory results may not be obtained simply by reducing the overall number or volume fraction of inclusions, unless the segregation of inclusions is also avoided. It has often been shown that anisotropy can be reduced by a high-temperature homogenizing treatment which reduces segregation and spheroidizes the inclusion stringers. However, this is generally an impractical solution due to the accompanying disadvantages such as oxidation and grain growth. Grange[35] developed a short-time, high-temperature treatment that eliminated ferrite-pearlite banding without markedly changing the shape of the inclusions, allowing him to compare the effects of inclusions in one steel in the banded and unbanded condition. When many elongated inclusions were present, removal of banding did little to improve transverse ductility. In the absence of inclusions removal of banding improved transverse ductility (reduction of area in a tensile test). Menter[36] performed hot notch tensile tests on specimens from segregated and unsegregated billets of En31 and confirmed the poor hot ductility associated with the former (Fig. 2.9).

Grange[35] realized that a few percent of martensite in banded steel is concentrated in relatively few bands, whereas when banding is removed, the same amount of martensite will be present as randomly dispersed small particles. The Hoggart[30], showed that a large and rapid plastic deformation of an inhomogeneous material may give rise to the following effects:

(a) stress gradients or discontinuities,
(b) interfacial stresses,
(c) crack or cavity formation,
(d) inhomogeneity of deformation,
(e) structural inhomogeneity,
(f) residual stresses.

A shear stress on a material may cause plastic flow, tensile fracture, or shear fracture, but, in an inhomogeneous material, fracture in one component or portion of the material may occur before it commences to deform plastically. If the strain in a material is homogeneous, the stress field for a homogeneous material is uniform; but this is not the case for an inhomogeneous material as the stress to cause a particular strain depends on the "stiffness", that is, the resistance to deformation of the material. Because the stress field in an inhomogeneous material must vary, stress gradients will occur and, if the inhomogeneity is discontinuous, a stress discontinuity will occur at the boundary so that interfacial stresses are generated. For a given strain, the magnitudes of the stress gradients, discontinuities or interfacial stresses depend on the stress differences and also on the relative sizes of the inhomogeneous regions.

Fig. 2.9: Comparative hot ductility of segregated and unsegregated casts of En31 steel shown by the reduction in area during hot notched tensile test (after Menter[36]).
Solute segregation in the weld can lead to variations in mechanical properties throughout the weldment and also to the occurrence of a range of weld metal defects including porosity and solidification cracking. It can affect the strength and response of a non-transformable weld deposit to post weld heat treatment, or where solid-state transformation occurs after solidification, can alter the form of the final microstructure of the weld bead. Under particular welding conditions and with particular consumables, low- and high-carbon martensites and bainitic carbides form in groups of islands along the prior solidification boundaries. This produces a marked decrease in as-welded impact strength [37]. Moreover, there is a pronounced tendency for alloying and impurity elements to segregate to the weld centre line where the columnar grains growing from each side impinge, which in turn may produce hot tearing as a result of low-melting eutectics between the dendrite arms.

2.5 Heterogeneity and Phase Transformations

Austenite decomposition kinetics are affected by numerous factors, including chemical free energy changes produced by alloy combinations, the influence of alloying elements on the solubility of carbon in γ, the morphology and type of carbides that precipitate and their spacing, the changes occurring in the composition of the γ as ferrite forms during the bainite transformation, the effects of dislocations created during phase transformations, and probably other factors that are not as obvious. Small changes in chemical composition can vary the kinetics of transformations, as well as, the kind and volume fractions of transformation products. In mild and low alloy steel weld metal, a relationship is clearly apparent between the segregation associated with the extended cellular-dendritic growth characteristic of these materials and the formation of low-temperature transformation products and, in particular, low- and high-carbon martensites [37,38]. Davenport [39] determined the isothermal transformation curves of three different steels that showed banding behaviour. The isothermal transformation curves of these steels in both the homogenized and un-homogenized conditions are shown in figures 2.10-2.12.

For homogeneous alloys, the time interval between the beginning and end of transformation was appreciably smaller than for the corresponding heterogeneous alloys. For the un-homogenized material, the transformation start curves should be representative
Fig. 2.10: Comparative isothermal transformation curves for S.A.E. 4640 (Fe-0.36C-0.63Mn-0.19Si-1.84Ni-0.06Cr-0.23Mo wt. %) before and after homogenization (after Devenport[39]).

of only the solute-depleted regions, while the transformation finish curve should be representative of only the high alloy solute-enriched regions.

Grange[35] observed the effect of banding in Fe-0.25C-1.5Mn wt. % steel on transformation of austenite. His results are summarized in figure 2.13. At all temperatures, transformation began slightly sooner in the steel without banding although no explanation is given for this. In fact, the primary phase to solidify in that investigation[35] was \( \gamma \) while in Davenport's investigation the primary phase was \( \delta \). He also observed, in agreement with Davenport[39], that above about 595°C this overall trend was reversed and completion was retarded in the steel without banding.

Farrar[40] has shown that in austenitic stainless steels the transformation at service temperature is strongly dependent on the original segregation of Cr, Mo and Ni in the as-welded condition. Depending upon the localised segregation within the \( \delta \)-ferrite laths they can exist in different parts of the Fe-Cr-Ni ternary phase diagram. If the initial segregation values allow the material to exist in the \( \delta + \gamma + \sigma \) phase field then the transformation is slow and the bulk of the ferrite is converted to carbides. but if
Fig. 2.11: Comparative isothermal transformation curves for S.A.E. 4140 (Fe-0.37C-0.77Mn-0.15Si-0.04Ni-0.98Cr-0.21Mo wt. %) before and after homogenization (after Devenport[39]).

Fig. 2.12: Comparative isothermal transformation curves for S.A.E. T-1335 (Fe-0.35C-1.85Mn-0.19Si wt. %) before and after homogenization (after Devenport[39]).
Fig. 2.13: Effect of banding on isothermal transformation of austenite in Fe-0.25C-1.5Mn wt. % steel (after Grange\textsuperscript{[35]}).

the material exists in the $\gamma + \alpha$ phase field the transformation is rapid and the majority of the ferrite is converted to $\sigma$ phase. Alfred Goldberg\textsuperscript{[41]} found the development of martensite in a heterogeneous maraging steel to occur by the formation of layers as the transformation progressed. This layer formation which has been shown to be responsible for the anisotropic transformation strains, was attributed to the presence of banded segregation which caused the transformation to occur along layers in the parent phase. This was particularly evident for the austenite to martensite transformation which continued to completion by the lateral growth of these layers. The layer structure was revealed by intrupting the austenite to martensite transformation during cooling, reheating to age the martensite that has formed, and then allowing to cool to ambient temperature to complete the transformation of the residual austenite to unaged martensite. Wu \textit{et al.}\textsuperscript{[34]} have also mentioned that the ferrite-pearlite banding can be eliminated apparently when the cooling rate is higher than a critical value. The critical cooling rate was found to be inversely proportional to the square of interband distance. On cooling below this critical rate, the strength of steel increases rather rapidly with increasing cooling rate. At higher cooling rates, the strengthening effects are less pronounced.
The extent to which segregation affects the final microstructure is also determined by the austenite grain size and cooling rate through transformation. The incidence of banding may be related to the local effects of the segregants on ferrite nucleation and carbon diffusion. Phosphorus contributes to ferrite banding by raising the temperature of ferrite formation, but since nucleation is delayed, the effect is suppressed by fast cooling rates. An austenite grain structure coarse in proportion to the segregant distribution pattern minimizes banding at a given cooling rate by providing ferrite nucleation sites which traverse segregated and unsegregated regions. The metallographic method of estimating the progress of transformation is particularly sensitive to such inhomogeneity in composition as one microscopic area in a specimen frequently showing almost complete transformation while an adjacent area may scarcely show even the beginning of transformation. Such a state of affairs makes estimation of the progress of transformation, for the steel as a whole, very difficult indeed. For heterogeneous steels, it is not obvious how the maximum volume fraction of ferrite that can be obtained by isothermal transformation in the $\alpha + \gamma$ phase field should differ from the corresponding maximum volume fraction of ferrite obtainable in a homogeneous steel of the same composition. There is experimental evidence\textsuperscript{[42]}, that the maximum volume fraction of allotriomorphic ferrite obtained by prolonged isothermal transformation in a heterogeneous steel does not vary linearly with the average carbon content of the steel concerned. This implies that the lever rule is not valid for heterogeneous steels. Bhadeshia\textsuperscript{[43]} looked into the effect of chemical heterogeneity on the formation of allotriomorphic ferrite by representing the banding as a composition wave of triangular shape and wavelength $\lambda$ at constant amplitude. He showed that the final volume fraction of $\alpha$ obtained at any temperature is independent of $\lambda$. However, while comparing the homogeneous and heterogeneous materials, we should be more concerned with the amplitude of the wave representing the variation of composition. Let wave A be represent the Mn concentration gradient in a heterogeneous material, and another wave B of smaller amplitude that for a relatively less heterogeneous material. Notice that the mean composition in the two situations are identical. This is illustrated in the Fig. 2.14, with the coordinate Z defined to be normal to the plane of constant composition in the specimen, that is normal to the plane of the diagram. Z is normalised to have a value of unity, equivalent to the total length of the specimen in the Z direction.
Fig. 2.14: Simulation of banding. The co-ordinate Z is defined to be normal to the planes of constant composition and is normalised with respect to the specimen length in the Z-direction. The curves A and B represent Mn concentration gradients in the banded steel. Vertical dotted lines show the volume fraction of ferrite represented by the position of interface for the two composition waves. Three different positions of the interface are shown in the figure:

(a) when $Mn < \overline{Mn}$,

(b) when $Mn = \overline{Mn}$,

(c) when $Mn > \overline{Mn}$. 
Fig. 2.15: Calculated isothermal sections of the Fe-Mn-C phase diagram, including the equilibrium and paraequilibrium phase boundaries. The tie-lines are for the equilibrium case, since those for paraequilibrium are all nearly parallel to the horizontal axis (after Bhadeshia\textsuperscript{[43]}).

The formation of ferrite is expected to cease when $x_\gamma = x_\gamma^\alpha$. For the heterogeneous alloy under consideration, $x_\gamma^\alpha$ varies with the position of the interface, since the Mn level also varies with $Z$. $x_\gamma^\alpha$ is therefore a function of $V$ and the condition for the reaction to cease may be written as:

$$x_\gamma^\alpha \{V\} = x_\gamma \{V\} \quad (2.9)$$

Where $x_\gamma^\alpha$ and $x_\gamma$ are implied to be function of $V$, by using the curly brackets. The two sides of this equation can be separately evaluated (using Fig. 2.15 and equation 2.8) and each plotted as a function of $V$, as shown in Fig. 2.16, where the calculations are carried out for steels with three different carbon concentrations, and for isothermal transformation at three different temperatures in the $\alpha + \gamma$ phase field.

Curves such as 'ab' represent $x_\gamma^\alpha \{V\}$ and the curves 'cd' represent $x_\gamma \{V\}$. Each intersection is a solution to equation 2.9, and gives a value of the Mn concentration at the position where the interface stops is $[0.8 + (1.2 - 0.8)V_{ht}]$ since $\text{Mn}_{\text{min}}$ and $\text{Mn}_{\text{max}}$ (see figure 2.14) were taken to be 0.8 and 1.2 wt.% respectively. Each open circle in figure 2.16 represents the value of $V_{hm}$ for a homogeneous steel containing 1.0 wt% Mn which is equal to the mean Mn level, $\overline{\text{Mn}}$, of the heterogeneous steel. To note the
difference between the transformation behaviour in homogeneous and heterogeneous steels, each open circle should be compared with the nearest intersection between curves of type 'ab' and 'cd'. This gives the corresponding values of $V_{hm}$ and $V_{ht}$. It is evident from the above discussion that there are circumstances when $V_{ht} > V_{hm}$, and also cases where $V_{ht} < V_{hm}$. The former occurs when the interface stops at a point where the Mn level is less than Mn and the latter when this Mn level is greater than Mn. When heterogeneous steels are heat-treated at relatively large undercoolings, such that the volume fraction of ferrite obtained is high enough to allow the transformation interfaces to stop at points where Mn > Mn, the actual volume fraction of $\alpha$ obtained will be less than that expected for homogeneous alloy. There will be no difference in $V_{ht}$ and $V_{hm}$ when Mn concentration at the interface equals Mn. The linear variation of $(1 - V_{hm})$ with $\overline{\chi}$ implied by the lever rule will clearly not be valid for heterogeneous steels; $(V_{ht} - V_{hm})$ depends on the absolute value of $V_{ht}$, which is in turn a function of $\overline{\chi}$. For any particular temperature, higher carbon steels lead to the formation of lower quantities of $\alpha$ before reaction ceases, and the interface is then more likely to stop at a position where Mn > Mn. This would lead to a higher than expected quantity of $\alpha$ so that the curve $(1 - V_{ht})$ versus $\overline{\chi}$ would tend to have a decreasing positive slope with increasing $\overline{\chi}$, in agreement with the work of Speich and Miller\textsuperscript{[42]}. 

**Fig. 2.16: Plot to determine the solution of equation (after Bhadeshia\textsuperscript{[43]}).**
Gretoft et al. [45] presented a modified computer model for the prediction of microstructure in low alloy steel weld deposits to account for the presence of solidification-induced alloying element segregation. The new model was tested on Fe-Mn-Ni-Si-C alloys and the results indicate that segregation can significantly increase the amount of allotriomorphic ferrite in the microstructure by making its nucleation relatively easy. It is because the driving force for $\gamma$ to $\alpha$ transformation is the highest in the solute depleted regions where $\alpha$ nucleation should first occur. In these circumstances, the major influence of segregation should be to raise the temperature at which $\alpha$ first forms. For given cooling conditions, the $\alpha$ then has more time to grow and the heterogeneous alloy should therefore have a higher volume fraction of $\alpha$. This is correct if the first phase to solidify is $\delta$, since the $\delta/\delta$ boundaries (where the last solute-rich liquid solidifies) are solute-rich. On further cooling, allotriomorphic $\gamma$ nucleates at the $\delta/\delta$ boundaries and when the $\delta$ to $\gamma$ reaction finishes, many of the $\gamma/\gamma$ columnar-grain boundaries ideally lie along the centre of the prior $\delta$ grains; the solute-depleted regions will therefore be at such $\gamma/\gamma$ boundaries (Fig. 2.17). If the first phase to solidify is $\gamma$ on the other hand, then solute segregation should make $\alpha$ nucleation more difficult.

Fig. 2.17: Schematic illustration of austenite grains crossing primary delta ferrite grain boundaries.
2.5.2 Cooling Rate and Inhomogeneity

Collins\textsuperscript{[46]} observed that by increasing cooling rate not only the microstructure is refined but the temperature range over which most of the transformation occurs is narrowed producing a more uniform microstructure instead of ferrite-pearlite banding. Such microstructural banding is due to inhomogeneous nucleation of ferrite and is usually attributed to segregation of Mn and other elements, which leads to enhanced ferrite nucleation in the Mn-depleted regions and low temperature products in the Mn rich-regions. Regardless of the origin of the initial nucleation rate inhomogeneity, the diffusion of carbon ahead of the $\gamma/\alpha$ interface into regions at which nucleation occurs at lower temperature further suppresses the transformation temperature in this region. Increased cooling rate reduces the time interval between nucleation at the most potent nucleation sites and the onset of transformation at less active sites. Consequently, the extent of ferrite growth from the most potent nucleation sites and the accompanying carbon segregation is reduced. Nucleation may occur at less active sites before carbon level begins to rise. Thus, with accelerated cooling rates, ferrite nucleation occurs more uniformly throughout the steel and the development of carbon rich regions or bands is reduced or eliminated. Tamehiro et al.\textsuperscript{[47]} have shown (Fig. 2.18) that the carbon distribution of the accelerated cooled plate is fairly uniform compared with that of the controlled rolled plate, though the concentration of Mn, P and other elements is the same for both plates.

The enrichment of carbon in the segregated zone of the controlled rolled plate occurs due to a lower cooling rate after rolling, because the segregation of Mn and other elements retards $\gamma$ to $\alpha$ transformation in the segregated zone, thus facilitating diffusion of carbon from the non-segregated area to the segregated zone. In the case of the accelerated cooled plate with a higher cooling rate, however, such a diffusion of carbon is suppressed and a banded microstructure disappears\textsuperscript{[47]}, as illustrated in Fig. 2.19.
Fig. 2.18: Distribution of carbon concentration in segregated zones of an accelerated cooled plate and a controlled rolled plate (after Tamehiro et al. [47]).

Fig. 2.19: Microstructural change of plate with accelerated cooling after controlled rolling (after Tamehiro et al. [47]).

(a) Controlled rolled plate.

(b) Plate after accelerated cooling.
REFERENCES


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Chapter 3
EXPERIMENTAL TECHNIQUE

3.1 Materials

The materials used in this work are as follows:

- **300M** has a typical composition of a low alloy steel (300M) containing Fe-0.45C-1.70Si-0.70Mn-1.90Ni-0.80Cr-0.40Mo-0.10V wt.%. During manufacture electrodes were produced from basic electric arc vacuum degassed steel, which were then vacuum arc remelted to 406 mm diameter ingot. The ingot was then annealed and forged on a precision forging machine to 135 mm square bar. The maximum forging temperature used was 1150 °C. It was then further annealed at 650/700 °C.

- **US83** and **US24** are of compositions Fe-0.20C-0.63Si-2.80Mn-0.04Ni-0.01Mo-1.10Cr wt.% and Fe-0.18C-0.75Si-1.98Mn-0.02Ni-0.01Mo-1.33Cr wt.% respectively. The steels were produced as electric furnace heats and continuously cast into 178 x 178 mm billets. These billets were reheated to 1232 °C, rolled to 22 mm diameter rods and air cooled. The steels are described as “air hardening” steels because of the mixed bainite/martensite/austenite microstructure which results after rolling and air cooling. These samples were produced by Inland Steel.

- **BS** is a badly segregated structural steel of average composition Fe-0.17C-0.85Si-1.38Mn wt.%.

3.2 Heat-Treatment

The aim of this work was to study the differences in transformation behaviour between chemically heterogeneous and homogeneous steels. To produce homogeneous samples, some of the steels were annealed at 1300 °C for three days. A vacuum furnace was used for this heat-treatment. In some cases, specimens were sealed in silica tubes under a partial pressure of argon in order to prevent oxidation and decarburisation. The silica tube was flushed three times with argon in each case, before sealing. The temperature was in all cases measured, using a Pt/Pt13 wt.% Rh thermocouple, at the specific position in the tube furnace where the specimens were located.
3.3 Optical Microscopy

Optical microscopy was used to observe the heterogeneity of microstructure after a variety of heat treatments. The specimens were hot mounted in acrylic plastic, and ground on silicon carbide paper to a sufficient depth to remove any unrepresentative surface. They were then mechanically ground down to 1200 grade emery paper and finally polished with 6, 1 and \( \frac{1}{4} \) micron diamond pastes. Picral, sodium metabisulphite and 2% Nital were used as etchants for different purposes throughout this work. Photography was carried out using an Olympus camera fitted to an Olympus microscope.

3.4 Dilatometry

Transformation can be detected as it happens using precision dilatometry, which is capable of sensing volume or heat capacity changes during the course of phase transformations. For this purpose a high speed dilatometer (Theta industries) was used, fitted with a water cooled radio frequency furnace. Nickel plated specimens were used throughout to avoid decarburisation. Nickel plating was carried out in two stages, i.e. striking and plating. Striking was carried out in a solution made up of 250g nickel sulphate, 27ml concentrated sulphuric acid and water, amounting to one litre in all. The solution was used at 50 °C, with a current density of 7.75 mA/mm\(^2\), for three minutes. The plating solution consisted of 140g nickel sulphate, 140g anhydrous sodium sulphate, 15g ammonium chloride and 20g boric acid, made up to one litre with distilled water. The plating was carried out at 50 °C, with a current density of 0.4mA/mm\(^2\) for fifteen minutes, to give a plate thickness of approximately 0.08 mm.

A "Data-Trak Programme", which is a pre-programmed heating schedule, was used for heating the specimen to the austenitizing temperature. For isothermal studies, a manual temperature control device was used to quench the specimen from its austenitizing treatment temperature to the pre-set transformation temperature. Rapid quenching was achieved by flushing with He gas. Any change in length of the specimen is transmitted to the transducer and nominally magnified 10\(^4\) times. The length transducer on the dilatometer was calibrated using pure platinum specimen of known thermal expansion characteristics. Data consisting of time, temperature and relative length change are collected on a floppy disc using a BBC microcomputer attached to the dilatometer. Both change in length and temperature were also monitored on a chart recorder which
moves at a pre-set speed.

3.5 Microhardness Testing

Microhardness measurements were made on polished and etched specimens using a Leitz hardness measuring digital eyepiece with the option of Vickers hardness tester to which a computer-counter-printer was attached. The indentation load applied for indentation was 0.981 N in each case. All the measurements were made at a suitable distance from the specimen edge. At least twenty readings were taken per specimen. In the case of heterogeneous specimens, measurements were made both along and across the segregation bands.

3.6 Microanalysis

Microanalysis experiments were carried out using energy dispersive X-ray analysis (interaction volume approximately 4.5 $\mu^3$) on a scanning electron microscope. The data obtained were analysed using the LINK microanalysis programme which corrects for the following effects:

- **Fluorescence i.e.,** photoelectric effect leading to secondary ionisation,
- **Atomic Number i.e.,** emitted X-ray intensity is affected by mass of sample penetrated by electrons, moreover, backscattering increases with increasing atomic number,
- **Absorption i.e.,** X-ray partially absorbed due to photoelectric effect.

3.7 Transmission Electron Microscopy

Philips EM300 and 400T electron microscopes were used for the examination of thin foils. The operating voltage was 100 kV and 120 kV respectively. Thin foil specimens were prepared for transmission electron microscopy from 0.25mm thick discs slit from specimens used in the dilatometric experiments. The discs were thinned down to 0.05mm by abrasion on silicon carbide paper and then electropolished in a twin jet electropolisher using a 5% perchloric acid, 25% glycerol and 70% ethanol mixture.
4.1 Introduction

300M is a medium carbon steel alloyed with several substitutional solutes and has a typical chemical composition Fe-0.45C-1.7Si-0.7Mn-1.9Ni-0.8Cr-0.4Mo-0.1V wt.%. The different alloying elements have many purposes\(^{[1-4]}\), but they all serve to enhance hardenability to such an extent that a 10cm diameter bar can be air cooled to a uniform martensitic microstructure. Molybdenum also helps to limit impurity-controlled temper embrittlement effects, and nickel has an intrinsic beneficial influence on the toughness of the martensite\(^{[1]}\). Vanadium serves to restrict austenite grain growth during the austenitising heat-treatment, usually carried out at a temperature not high enough to completely dissolve particles of vanadium carbides. The composition is in fact based on the popular “4340” steel which acquires its optimum strength and toughness in the quenched and tempered martensitic condition. The 4340 steel unfortunately suffers from tempered martensite embrittlement, in which the toughness goes through a minimum at a tempering temperature of \(\approx 300 \, ^\circ\text{C}\). At low tempering temperatures the cementite particles are too fine to be detrimental. Although at high tempering temperatures they are relatively coarser, the yield strength is by then rather low so that the material can accommodate coarser particles. It is at the intermediate temperatures where the curve of toughness versus tempering temperature shows a minimum that there is an unfavourable combination of cementite particle size and yield strength. The 300M steel was designed to avoid this problem by increasing the silicon concentration to a level high enough to retard the coarsening of cementite, and hence to shift the toughness minimum to a higher tempering temperature. It can therefore be tempered at a relatively low temperature and hence avoid the large loss of strength associated with tempering at elevated temperatures\(^{[1-3]}\).

Both 4340 and 300M steel are best utilised in the quenched and tempered condition. When attempts are made to use 4340 steel in a bainitic condition, the toughness obtained is not impressive because of the coarse cementite particles associated with upper bainite in this medium carbon steel. On the other hand when 300M steel is
isothermally transformed to upper bainite, cementite does not readily precipitate and the microstructure then contains only bainitic ferrite and residual austenite at the isothermal transformation temperature. This is due to the high silicon concentration which severely retards the precipitation of cementite from the residual austenite. However, the toughness in the isothermally transformed 300M steel is still poor compared with that associated with tempered martensite, because some of the carbon-enriched residual austenite transforms to high-carbon, untempered martensite during cooling to ambient temperature. Furthermore, the austenite retained at ambient temperature is unstable to stress-induced martensitic transformation, a phenomenon which in this instance is detrimental since the energy absorbed by the transformation is inadequate to compensate for the brittle nature of the transformation product.

If the mechanical stability of the residual austenite in isothermally transformed 300M steel could be improved, the resulting microstructure of just bainitic ferrite and stable retained austenite should have a good combination of strength and toughness, since the ultrafine-grained body-centered cubic (BCC) platelets of bainitic ferrite are then separated by tough and inherently more ductile films of stable face-centered cubic (FCC) austenite. It has been demonstrated that the structure of high-silicon bainitic steels can be optimised by using phase transformation theory. If it is assumed that the growth of bainite is diffusionless, but that the carbon is partitioned into the residual austenite immediately after transformation, then the bainite reaction should stop when the carbon concentration of the residual austenite reaches the $T_o$ curve on the phase diagram.

The $T_o$ curve defines the locus of all temperatures at which austenite and ferrite of the same chemical composition have the same free energy (see for example); hence, diffusionless growth of bainite is thermodynamically impossible if the carbon concentration of the austenite exceeds that given by the $T_o$ curve at the appropriate transformation temperature. In fact, the growth of bainite is accompanied by a shape deformation which has to be accounted for in deciding the thermodynamic criteria for

*Throughout this chapter, the term “residual austenite” refers to the austenite that exists at the reaction temperature during isothermal transformation to bainite, whereas the term “retained austenite” refers to the austenite which remains untransformed after cooling the specimen to ambient temperature.
growth. The $T'_0$ curve, which also allows for the stored energy due to transformation (estimated to be about $400\, \text{J/mol}^{-1}$ for bainitic ferrite[13]), gives the more appropriate condition for the formation of bainite. It will later also be necessary to consider the $A'_{e3}$ curve, which is the paraequilibrium $\alpha + \gamma/\gamma$ phase boundary. Note that much of the stored energy arises from the strain energy due to the invariant-plane strain shape change accompanying transformation. The calculation of the strain energy is carried out for an isolated plate which grows under purely elastic constraint. Plastic accommodation effects and elastic interactions between plates will in reality reduce the value of stored energy.

A more stable austenite is obtained if the $T'_0$ curve is shifted towards higher carbon concentrations[7,8]. The position of the $T'_0$ curve is determined by the thermodynamics of the BCC and FCC solid solutions, since it gives the locus of all temperatures where austenite and ferrite of the same composition have equal free energy. Hence, the microstructure of silicon steel can be controlled using the thermodynamic theory of the bainite transformation.

The concepts discussed above have been tested successfully for a range of high-strength steels[7-11]. However, the theory is strictly applicable only to chemically homogeneous steels. On the other hand, most commercial steels are to some extent chemically heterogeneous, and it is certainly common to observe a banded bainitic microstructure in isothermally transformed 300M steel. The purpose of the present work was to develop phase transformation theory to enable the prediction of the extent of bainitic transformation in chemically heterogeneous high-silicon steels. The work is a part of a general programme on modelling the development of microstructure in low-alloy steels.

4.2 Results and Discussion

Microanalysis was carried out on heterogeneous samples austenitised at 950 °C for 10 min and isothermally held at 400 °C until the transformation ceased. Light microscopy revealed a heavily banded microstructure consisting of (solute-depleted) regions which are predominantly bainitic, separated by bands of predominantly martensitic microstructure (Fig. 4.1a, b).
The microanalysis data are presented in Fig. 4.2 where the regions designated "matrix" were essentially untransformed at the isothermal transformation temperature and are seen to be significantly richer in substitutional alloy concentration. The range of concentration variation was found to be approximately 1.55-1.97Si, 0.56-0.89 Mn, 1.74-2.06 Ni, 0.35-0.88 Mo, 0.77-1.44Cr and 0.0-0.18 V, wt.%. Since the microanalysis technique draws information from an interaction volume which is about $4.5 \mu m^3$, the actual variations in solute concentrations may be underestimated in the data of Fig. 4.2. An underestimation of this kind should lead to a large error in any attempt at calculating the nucleation rate of bainite in the heterogeneous samples, since the size of the nucleus is likely to be much smaller than the interaction volume. However, the main aim of the present work is to examine the limiting volume fractions of bainite obtained after prolonged isothermal transformation. Since the volume of a sheaf of bainite is expected to be much larger than the interaction volume, any error resulting from the spatial resolution of the microanalytical technique, in calculating the limiting volume fraction of bainitic ferrite should be negligible. Note also that it is not necessary to consider an inhomogeneous carbon distribution in the austenite at 950 °C since the diffusivity of carbon in austenite is very large at that temperature. This does, however, involve the approximation that during austenitisation, it is the concentration of carbon which is uniform throughout, instead of its activity. The latter is a function of the substitutional solute concentration, which in turn is not constant.

On the other hand, for dilute steels such as the 300M steel used here, it is unlikely that the concentration of carbon varies significantly within the austenite at 950 °C. This is verified by the uniformity of hardness data (Fig. 4.3) from fully martensitic specimens obtained by quenching into iced-brine following austenitisation at 950 °C for 10 mins. The load used for hardness testing was such that the indent size was less than about half the typical microstructural band width.

With the exception of silicon, all of the elements Ni, Mn, Mo, V and Cr are expected to retard the bainite reaction as illustrated in Fig. 4.4 which shows time-temperature-transformation (TTT) diagrams for hypothetical steels of composition similar to 300M, calculated using the method of Bhadeshia\cite{14,15}. The effect of an excess addition of 1wt.% of each alloying addition is examined (for silicon, the excess addition is 2wt.%
in order to produce a discernable effect). Based on these data, it is expected that the solute depleted regions should transform first.

Fig. 4.5 shows a typical dilatometric plot of the change in relative specimen length as a function of temperature during cooling from the austenitising temperature to the lowest isothermal transformation temperature used in the present experiments. The linearity of the plot proves the lack of any transformation during the quench to the isothermal transformation temperature.

Isothermal transformation experiments were carried out over the temperature range 440-320 °C, for both the homogenised and as-received samples. Typical microstructures, as characterised using transmission electron microscopy are illustrated in Figs. 4.6 and 4.7. Carbide-free upper bainite was obtained in all cases except for transformation at 320 °C, where a small amount of lower bainite (Fig. 4.7) was also observed. As with the upper bainite obtained by transformation at higher temperature, austenite was also found between the subunits of lower bainite. Since the presence of lower bainite is not accounted for in the calculations; the carbide particles in the lower bainite in effect remove carbon from the system, the results of the theoretical analysis of the data obtained from the 320 °C experiments are treated with caution.

4.2.1 Dilatometric Analysis

The results of isothermal transformation experiments are presented in Fig. 4.8 and supported by metallographic evidence (Fig. 4.9). As expected, the curves are all of sigmoidal shape, the extent of transformation reaching some maximum value, denoted by a maximum length change \( (\Delta l/l)_m \) on prolonged holding at the isothermal transformation temperature. The length change obtained in the dilatometric experiments can be related to the volume fraction of upper bainite \( V_b \) obtained as follows:

\[
\frac{\Delta l}{l} = \frac{2V_b a_\alpha^3 + (1 - V_b) a_\gamma^3 - \overline{a}_\gamma^3}{3\overline{a}_\gamma^3} \tag{4.1}
\]

where \( a_\alpha \) is the lattice parameter of ferrite at the transformation temperature, given by:

\[
a_\alpha = a_\alpha^0 [1 + e_\alpha (T - 25)] \tag{4.2}
\]

and \( \overline{a}_\gamma \), which is the lattice parameter of austenite of the alloy composition at the transformation temperature, is given by:

\[
\overline{a}_\gamma = (a_\gamma^0 + \Sigma c_i x_i)[1 + e_\gamma (T - 25)]. \tag{4.3}
\]
In these equations, $\varepsilon_a$ and $\varepsilon_\gamma$ represent the linear thermal expansivities of ferrite and austenite respectively, $a_o$ is the lattice parameter of austenite in pure iron at 25 °C, $x_i$ is the concentration of alloying element $i$ and $c_i x_i$ represents the change in $a_o$ due to the addition of the alloying element to pure iron. $T$ is the temperature in °C. Values of $\varepsilon_a$, $\varepsilon_\gamma$ and $a_o$ are given by $1.1103 \times 10^{-5} \text{K}^{-1}$, $1.7951 \times 10^{-5} \text{K}^{-1}$ and $0.28661 \pm 0.0001nm$ respectively\[16]. The coefficients $c_i$ and the parameter $a_o'$ is from the work of Dyson et al. \[17].

After making the appropriate substitutions, the above equations can be solved to give the volume fraction of bainite (Table 4.1) and the carbon concentration of the residual austenite. In this way, the carbon concentration in the austenite at the point where isothermal transformation ceases can be calculated, and a comparison of such data for upper bainite, with the $T_o$, $T'_o$ and $A'_e\text{3}$ curves, calculated for the chemical composition of the homogeneous alloy, is presented in Fig. 4.10.

If the growth of bainite is assumed to be diffusionless, and carbon is subsequently partitioned into the residual austenite, then in the absence of any other interfering reactions, the formation of bainite should cease when the carbon concentration of the residual austenite reaches somewhere between the limits defined by the $T_o$ and $T'_o$ curves. On the other hand if the bainitic ferrite does not form with any supersaturation of carbon then the reaction can in principle continue until the carbon concentration of the residual austenite reaches the paraequilibrium $A'_e\text{3}$ phase boundary. It is evident from Fig. 4.10 that the experimental data support the conclusion that the growth of bainite is diffusionless, with the carbon being partitioned subsequently into the residual austenite. Fig. 4.11 illustrates a similar comparison for the as-received (heterogeneous) sample of 300M steel, which was isothermally transformed to upper bainite. In Fig. 4.11, the calculations of phase boundaries cover the range of chemical compositions detected experimentally. The results are again consistent with the hypothesis that the growth of bainite is diffusionless. The results show that 300M steel accurately exhibits the incomplete reaction phenomenon, which can be used to estimate theoretically the degree of transformation expected as a function of isothermal transformation temperature or in terms of the detailed alloy chemistry. They also show that fully bainitic microstructures cannot be obtained in 300M steel by any heat-treatment, since the final microstructure obtained at ambient temperature is always expected to be some
mixture of bainite, high-carbon untempered martensite and carbon-enriched retained austenite. This has implications in the interpretation of microstructure/property data.

A further examination of the experimental data (Figs. 4.8-12, Table 4.1) shows that the maximum degree of transformation obtained at any isothermal transformation temperature is higher for the homogenised samples when compared with the as-received steel. The exception is at very low undercoolings below the $B_s$ temperature, where the degree of transformation is higher for the heterogeneous samples. The effect of chemical segregation in general is to reduce the degree of bainitic transformation.

The presence of solute depleted regions in the heterogeneous samples is expected to locally promote the formation of bainite at temperatures which are above $B_s$ for the homogeneous samples. This explains why at relatively high temperatures, the degree of transformation is lower in the homogenised samples. Metallography (Figs. 4.1 and 4.9) provides clues as to why the situation reverses when transformation is carried out at higher undercoolings below $B_s'$, with the homogeneous samples undergoing a higher degree of transformation at any given temperature. It is evident that in the homogeneous samples, the bainite nucleates uniformly at all locations, whereas in the heterogeneous specimens the substitutional-solute enriched regions do not transform at all. Furthermore, the untransformed bands in the latter specimens do not serve as sinks for the carbon that partitions from the bainitic ferrite, since most of that carbon is likely to be trapped in regions between the bainite subunits. If the bands could act as sinks for carbon then this would permit further transformation in the substitutional-solute depleted regions. To explore these qualitative arguments in more detail, a computer model was designed to simulate the development of bainitic transformation in chemically heterogeneous steels.

4.2.2 Transformation Model

To model the transformation behaviour, the heterogeneous steel was represented as a composite of $N$ slices of equal thickness (Fig. 4.13). Each slice, identified by a subscript $i$, was assigned a different chemical composition consistent with the experimental measurements of composition as a function of distance. The composition within the slice was set to be uniform. The mean composition of all the slices was identical to the mean composition of the as-received 300M steel.
The calculation was carried out in stages, with each stage identified by the subscript $j$. For each value of $j$ (i.e., at each stage of the calculation), the volume fraction of bainite in each slice was incremented by a small fraction $\Delta V$, provided transformation is thermodynamically feasible in that slice. Since bainite has to nucleate at the beginning of transformation in any slice, the condition for detectable nucleation of bainite is given by simultaneously satisfying the equations:

$$\Delta G^\gamma-\gamma^+ \alpha \leq \Delta G_N$$  \hspace{1cm} (4.4)$$

and

$$\Delta G^\gamma-\alpha \leq 0 \text{ J mol}^{-1}$$  \hspace{1cm} (4.5)$$

where $\Delta G^\gamma-\gamma^+ \alpha$ is the free energy change accompanying the nucleation of a very small amount of bainitic ferrite, and $\Delta G_N$ is the minimum free energy change that is necessary in order to obtain a detectable rate of nucleation$^{15,18}$; the function $\Delta G_N$ has been defined as:

$$\Delta G_N = 3.25175(T - 273.15) - 2183 \text{ J mol}^{-1}$$  \hspace{1cm} (4.6)$$

where the units of temperature are in Kelvin.

Equation 4.4 therefore defines the thermodynamic condition that has to be satisfied in order to obtain a detectable nucleation rate for bainite, and Eq. 4.5 defines the thermodynamic condition for growth to be feasible, i.e., that the driving force for diffusionless transformation to bainitic ferrite $\Delta G^\gamma-\alpha$ should exceed the stored energy of bainite. Simultaneous solution of the two equations gives the local bainite-start temperature for a given slice, $B_s^i$. Hence, at the beginning of transformation in a given slice, the calculated bainite-start temperature must be above the isothermal transformation temperature $T_i$ if that slice is to transform at all:

$$B_s^i > T_i$$  \hspace{1cm} (4.7)$$

Once the nucleation condition has been satisfied, the rules governing subsequent transformation can be less restrictive since only the growth condition (Eq. 4.5) needs to be satisfied. The formation of bainite involves diffusionless growth, but the excess carbon in the bainitic ferrite is immediately afterwards partitioned into the residual
austenite, so that at any stage of the reaction, the carbon concentration of the residual austenite \( x_\gamma \) changes with the fraction of transformation. Thus, the growth condition depends on the instantaneous value of \( x_\gamma \), so that an increment of volume fraction is only permitted if:

\[
x^{ij}_\gamma < x^{i}_{T_o}
\]  

(4.8)

where \( x^{i}_{T_o} \) is the concentration of carbon in slice \( i \) at temperature \( T_i \) where austenite and ferrite of the same composition have the same free energy. It is given by the \( T_o \) curve computed for the particular slice concerned.

The calculation begins with all slices being fully austenitic. For the first step \( (j = 1) \) \( B_s \) temperatures are calculated for all the slices. If for any slice, \( B^i_s < T_i \) then that slice remains untransformed throughout the experiment. For slices which are below their \( B^i_s \) temperatures, a small amount of bainite is permitted to form, giving a volume fraction increment of \( \Delta V \). This increment of transformation changes the carbon concentration in the unreacted regions of the slices according to the equation

\[
x^{ij}_\gamma = \bar{x} + \frac{V_{ij}(\bar{x} - x_\alpha)}{(1 - V_{ij})}
\]  

(4.9)

where \( V_{ij} \) and \( x^{ij}_\gamma \) are, respectively, the total volume fraction of bainitic ferrite, and the total carbon concentration of the residual austenite in slice \( i \) at stage \( j \) of the calculation. \( x_\alpha \) is the amount of carbon which is left in the bainitic ferrite, either in solid solution or in the form of carbides precipitated from supersaturated ferrite. Hence, for \( j > 1 \), an increment of transformation is only allowed in any given slice if for that slice \( x^{ij}_\gamma < x^{i}_{T_o} \). The mean volume fraction of transformation in the alloy as a whole at stage \( j \) is given by:

\[
\bar{V}_j = \frac{\sum_i V_{ij}}{N}.
\]  

(4.10)

The calculation is stopped when all slices cease to transform; \( x^{ij}_\gamma = x^{i}_{T_o} \) for all \( i \).

We consider first the case where the slices transform independent of each other, i.e., without any diffusion of carbon between slices. This is the more likely circumstance because the sheaf morphology of bainite in general ensures that regions of residual austenite are isolated from one another, so that carbon does not homogenise over large distances.
To decide on the number of slices into which the alloy should be divided, the calculations were carried out for several values of \( N \) (Fig. 4.14). The results of the calculations converged as \( N \) tended towards 100 (the curves for \( N = 80 \) and \( N = 100 \) are virtually identical in Fig. 4.14), so that all subsequent computations were carried out with \( N = 100 \). Fig. 4.15a illustrates how the number of non-transforming slices varies as a function of transformation temperature and the stage of the calculation. At higher transformation temperatures (i.e., lower driving forces), a large number of the substitutional-solute enriched slices are above the \( B_s \) temperature and do not participate at all in the transformation process. This is consistent with the observation of untransformed bands in the samples reacted at higher temperatures (Figs. 4.1 and 4.9). As the carbon concentration of the residual austenite increases during transformation and approaches the appropriate \( x_{T_o} \) value, there is for each transformation temperature an abrupt increase in the number of non-transforming slices (Fig. 4.15a). The slope of the last part of each curve in Fig. 4.15 is determined by the degree of inhomogeneity in the alloy; for a homogenous alloy it is expected to be infinite in slope.

The calculations use a finite increment \( \Delta V \) of transformation for successive stages of the reaction. Clearly, the precision of the method is expected to deteriorate as \( \Delta V \) increases; Fig. 4.15b illustrates how the calculated maximum volume fraction of transformation to upper bainite depends on the magnitude of the increment used. The variations in the calculated results are not large, but are significant at higher transformation temperatures where the absolute maximum volume fraction is in any case rather low, and the use of a large \( \Delta V \) also seems to give a lower degree of discrimination between the different transformation temperatures. For these reasons, all subsequent calculations were carried out using \( \Delta V = 0.00005 \).

The increase average carbon concentration of the residual austenite during the reaction is illustrated in Fig. 4.16, where the maximum value in each case is determined approximately by the \( T_o \) curve of the phase diagram; the values are not exactly determined by the \( T_o \) curve because each slice has a different substitutional alloy content (and hence a different \( T_o \) curve), so that the maximum value reflects an averaged effect.
4.2.9 Comparison between experiment and theory

Calculations of the maximum volume fractions of bainitic ferrite expected by isothermal transformation were carried out using the computer model described above, and compared with experimental data (Table 4.1) in Figs. 4.17a, b, c. The agreement is found to be reasonable, both in an absolute sense (Figs. 4.17a, b), and in predicting the different behaviours of the as-received and homogenised samples (Fig. 4.17c). For example, for most of the data, both theory and experiment show a higher degree of transformation in the homogenised samples, and both show a reversal of trend as the transformation temperature approaches the $B_s$ temperature of the homogenised alloy.

The fact that the homogenised samples in general show a higher degree of transformation when compared with the more heterogeneous samples was explained earlier on two grounds. Firstly, the nucleation of bainite occurs uniformly throughout the homogeneous samples, while it is restricted to the substitutional-solute depleted regions in the segregated samples. Secondly, since the carbon that partitions from the bainitic ferrite essentially remains trapped locally between the ferrite subunits, the untransformed regions of the heterogeneous sample which are rich in substitutional alloy content are unable to act as sinks for the excess carbon, so as to allow further transformation in the substitutional-solute depleted regions.

The significance of this last effect can be examined theoretically using the computer model with the additional condition that after every increment $\Delta V$ of transformation, the carbon is allowed to redistribute and homogenise between the slices. This should allow the substitutionally-enriched regions to act as sinks for excess carbon, thereby promoting further reaction in the substitutionally-depleted regions. The fact that the carbon does not homogenise during transformation is emphasised by the results presented in Figs. 4.17d and 4.17e, where the calculated data (assuming that carbon homogenises between the slices) are seen to overestimate the volume fraction of bainite.

The results (Fig. 4.17f) also show that if carbon is permitted to homogenise in the residual austenite after every increment of transformation, the volume fraction of transformation in the heterogeneous samples should always exceed that in the homogenised samples. This idea is difficult to test experimentally, because the nature of a bainite sheaf is such that film-like regions of austenite become trapped between the subunits of...
bainite. This isolates them from the other regions of austenite, thereby preventing the long-range homogenisation of carbon. On the other hand, if the transformation could be forced to proceed at a very slow rate, such that the time between the formation of successive subunits is large enough to allow the carbon to diffuse over long distances, then it would be experimentally possible to allow the substitutionally-enriched regions to act as sinks for the excess carbon. This was done by studying transformation behaviour, for both as-received and homogenised samples, during continuous cooling experiments. The experiments were based on the idea that as the samples cool through the transformation temperature range, they should experience small increments in transformation. If the cooling rate is sufficiently slow, it should permit substantial, if not complete, homogenisation of the rejected carbon.

The results of the continuous cooling experiments are presented in Figs. 4.18 and 4.19. The experiments were carried out at cooling rates between 6 - 215°C hr⁻¹. The results from the slowest cooling rate used confirm the theoretical prediction (Fig. 4.20) that if an opportunity is provided for carbon to homogenise in the residual austenite during transformation, then the heterogeneous samples should transform to a greater extent than those which are homogenised (Fig. 4.19). As the cooling rate increases, the possibility of long-range carbon diffusion diminishes and Fig. 4.19 shows that the results tend towards those obtained during isothermal transformation, i.e., the degree of transformation in higher in the homogenised samples at high undercoolings, the reverse being true at low undercoolings.

4.3 Conclusions

It has been demonstrated that when 300M steel is isothermally transformed to bainite, the kinetics and maximum extent of transformation are sensitive to the presence of relatively small levels of chemical segregation, of the kind commonly associated with commercial samples. During isothermal transformation at high undercoolings, the maximum degree of bainitic ferrite obtained is found to be larger for homogenised samples because bainite is able to nucleate uniformly throughout the samples and because the carbon that is rejected into the residual austenite after transformation is trapped by isolated regions of austenite. In the heterogeneous samples, the bainite nucleates mainly in the substitutional-solute depleted regions and furthermore, the
untransformed substitutional-solute enriched regions are unable to act as effectively as sinks for excess carbon, as would be the case if all regions of austenite were freely connected.

At very low undercoolings, the extent of isothermal transformation is found to be larger in the heterogeneous samples, since at such undercoolings, the transformation is nucleation dominated. Thus, regions of the heterogeneous samples are able to transform at temperatures above the bainite-start temperature of the homogenised alloy.

It has been shown that if an opportunity is provided for carbon to distribute evenly throughout the residual austenite during the development of the bainitic microstructure, then the extent of transformation is always larger for the heterogeneous samples when compared with the homogenised samples.

The experimental results have been rationalised using a theoretical model for the bainite reaction in heterogeneous steels. The model is based on the hypothesis that the growth of bainite is diffusionless, but that the excess carbon in the bainitic ferrite is immediately afterwards partitioned into the residual austenite.
Fig. 4.1: (a) Optical micrographs illustrating the banded microstructure obtained in the heterogeneous 300M steel after isothermal transformation at 400 °C (for 90 minutes) until reaction completion. (b) Corresponding optical micrograph for the homogenised sample of isothermally transformed 300M steel. For both samples, the dark etching regions are mainly bainitic and the lighter etching regions contain mainly untempered martensite, obtained during the quench from the isothermal transformation temperature.
Fig. 4.2: Microanalysis data from heterogeneous samples of 300M steel which were austenitised at 950 °C and then isothermally transformed at 400 °C (for 90 minutes) until reaction ceased. The regions designated "matrix" were essentially untransformed at the isothermal transformation temperature, whereas those designated "band" consisted predominantly of bainitic ferrite. The error bars indicate the typical 95% confidence statistical error and the average composition is in each case indicated by the dashed horizontal line.
Fig. 4.3: (a) Vickers Hardness tests (50g load) from a fully martensitic sample of homogenised 300M steel. (b) Vickers hardness tests (50g load) from a fully martensitic sample of heterogeneous 300M steel.
Fig. 4.4: Calculated time-temperature-transformation (TTT) diagrams (for reaction initiation) showing the influence of adding an excess of solute to the 300M steel of average composition as used in the present work. (a) Ni; (b) V; (c) Cr; (d) Mn; (e) Mo; (f) Si. The dashed curves represent the time taken to initiate transformation in 300M steel of the base composition, and the continuous curves for the steel with the relevant excess solute addition. The concentration of excess solute added is 1wt.% in all cases except Si, where a 2wt.% excess has been added in order to produce a discernable effect. Notice that in all cases (except Si), the bainite and martensite reaction are retarded by the extra solute addition.
Fig. 4.4: (continued ......) (c) Cr; (d) Mn; (e) Mo; (f) Si.
Fig. 4.5: Dilatometric curves showing the linear variation of relative specimen length as a function of temperature during cooling from the austenitising temperature to the isothermal transformation temperature. (a) Homogenised sample; (b) Heterogeneous sample.
Fig. 4.6: (a) Bright field transmission electron micrograph from a homogeneous sample of 300M steel, isothermally transformed to upper bainite at 400 °C for 90 minutes before quenching to ambient temperature. Shows sheaves of bainite consisting of subunits of bainitic ferrite separated by regions of retained austenite (and martensite); (b) corresponding retained austenite dark-field image.
Fig. 4.7: Mixed microstructure of upper and lower bainite obtained by isothermal transformation of homogeneous 300M steel at 320 °C for 60 minutes before quenching to ambient temperature. (a) Bright field image of upper bainite; (b) same sample, but showing lower bainite.
Fig. 4.8: Dilatometric curves for samples of 300M steel isothermally transformed at the temperatures indicated. The continuous curves are for the homogenised samples and the dashed curves for the heterogeneous samples. Data on the limiting volume fractions obtained are given in Table 4.1.
Fig. 4.8: (continued .... )
Fig. 4.9: Metallographic confirmation of the curves shown in Fig. 4.8.
(a) Optical micrograph of the homogeneous specimen isothermally transformed at 320 °C.
(b) Optical micrograph of the heterogeneous specimen isothermally transformed at 320 °C.
(c) Optical micrograph of the homogeneous specimen isothermally transformed at 340 °C.
(d) Optical micrograph of the heterogeneous specimen isothermally transformed at 340 °C.
Fig. 4.9: (continued.....)

(e) Optical micrograph of the homogeneous specimen isothermally transformed at 380 °C.

(f) Optical micrograph of the heterogeneous specimen isothermally transformed at 380 °C.

(g) Optical micrograph of the homogeneous specimen isothermally transformed at 420 °C.

(h) Optical micrograph of the heterogeneous specimen isothermally transformed at 420 °C.
Fig. 4.9: (continued ....)

(i) Optical micrograph of the homogeneous specimen isothermally transformed at 440 °C.

(j) Optical micrograph of the heterogeneous specimen isothermally transformed at 440 °C.

(k) Optical micrograph of the homogeneous specimen isothermally transformed at 460 °C.

(l) Optical micrograph of the heterogeneous specimen isothermally transformed at 460 °C.
Table 4.1: Dilatometrically determined maximum volume fractions of bainitic ferrite obtained by isothermal transformation at the temperatures indicated, for both the as-received and homogenised samples of 300M steel.

<table>
<thead>
<tr>
<th>Isothermal Transformation Temperature °C</th>
<th>Experimental Volume Fraction Homogeneous</th>
<th>Heterogeneous</th>
</tr>
</thead>
<tbody>
<tr>
<td>320</td>
<td>0.63</td>
<td>0.64</td>
</tr>
<tr>
<td>340</td>
<td>0.60</td>
<td>0.48</td>
</tr>
<tr>
<td>380</td>
<td>0.45</td>
<td>0.40</td>
</tr>
<tr>
<td>400</td>
<td>0.50</td>
<td>0.33</td>
</tr>
<tr>
<td>420</td>
<td>0.34</td>
<td>0.14</td>
</tr>
<tr>
<td>430</td>
<td>0.06</td>
<td>0.04</td>
</tr>
<tr>
<td>440</td>
<td>0.11</td>
<td>0.07</td>
</tr>
<tr>
<td>450</td>
<td>0.02</td>
<td>0.03</td>
</tr>
<tr>
<td>460</td>
<td>0.03</td>
<td>0.05</td>
</tr>
</tbody>
</table>

Fig. 4.10: Calculated $T_o$, $T'_o$, and $A_e$ phase boundaries for 300M steel. The experimental data are for samples transformed isothermally to upper bainite until reaction ceases.
Fig. 4.11: Calculated $T_o$ and $A'_e$ phase boundaries for heterogeneous 300M steel, covering the range of chemical compositions detected experimentally. The experimental data are for samples transformed isothermally to upper bainite until reaction ceases.

Fig. 4.12: A plot of the maximum volume fraction of bainitic ferrite obtained by isothermal transformation in homogenised 300M steel, versus the corresponding volume fraction for as-received 300M steel. The line has a slope of unity, and serves to illustrate that except at transformation temperatures near $B_s$ (where the degree of transformation possible is minimal), the extent of the transformation is larger in the homogenised samples.
Choose $T$, $N$

Set $V_i = 0$ For all $i$

Calculate $x_{T_i}B_i$ For all $i$

$V_i = x_i$

$B_i < T_i$

Yes

No

$x_{ih} < x_i$

Yes

No

$V_{ij} = V_{ij} + 0$

$V_{ij} = V_{ij} + \Delta V$

$i = i + 1$

Is $i = N$?

Yes

No

$V_j = \Sigma V_{ij} / N$

STOP

Have all slices stopped transforming?

Yes

No

$j = j + 1, i = 1$

Fig. 4.13: Flow chart illustrating the calculation procedure used to simulate the development of transformation in heterogeneous 300M steel. $T_i$ represents the isothermal transformation temperature and the subscript $i$ identifies the slice number and composition; the total number of slices is $N$. The calculation is carried out in stages, with each stage identified by the subscript $j$. For each value of $j$ (i.e., at each stage of the calculation), the volume fraction $V_{ij}$ of bainite in each slice is incremented by a small fraction $\Delta V$ if transformation is feasible in that slice. The total volume fraction of bainite at stage $j$ is thus given by $\Sigma_i V_{ij} / N$. 

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Fig. 4.14: Variation in the calculated maximum volume fraction of upper bainitic ferrite as a function of transformation temperature and the number of slices $N$ into which the heterogeneous alloy was rationally divided. Note that the calculations for $N$ values of 80 and 100 are virtually superimposed.
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Fig. 4.16: Variation in the calculated average carbon concentration of the residual austenite as a function of the stage of the calculation (j) and the isothermal transformation temperature, assuming that the transformation product is upper bainitic ferrite.
Fig. 4.17: Comparison of the calculated (under circumstances when carbon is not allowed to homogenise in the residual austenite after each increment of transformation) and experimental maximum volume fractions of bainitic ferrite for (a) the homogenised alloy; (b) for the as-received alloy; (c) comparison of the homogenised and as-received alloys, for both the calculated (no homogenisation of carbon) and experimental data. Comparison of the calculated (under circumstances when carbon is allowed to homogenise in the residual austenite after each increment of transformation) and experimental maximum volume fractions of bainitic ferrite for (d) the homogenised alloy; (e) for the as-received alloy; (f) comparison of the homogenised and as-received alloys, for both the calculated (homogenisation of carbon) and experimental data. For all the above data, the transformation temperatures are as listed in Table 4.1; note however that small maximum volume fractions correspond to transformation temperatures near to the $B_s$ temperature.
Fig. 4.17: (continued .....)

(c) comparison of the homogenised and as-received alloys, for both the calculated (no homogenisation of carbon) and experimental data. Comparison of the calculated (under circumstances when carbon is allowed to homogenise in the residual austenite after each increment of transformation) and experimental maximum volume fractions of bainitic ferrite for (d) the homogenised alloy; (e) for the as-received alloy; (f) comparison of the homogenised and as-received alloys, for both the calculated (homogenisation of carbon) and experimental data.
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Fig. 4.19: The information extracted from the data presented in Fig. 4.18, for the cooling rates 4, 0.35, 0.1833, 0.1 °C/min.
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REFERENCES


Chapter 5

KINETICS OF MARTENSITIC TRANSFORMATION IN PARTIALLY BAINITIC 300M STEEL

NOMENCLATURE AND ABBREVIATIONS

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a_\gamma)</td>
<td>Lattice parameter of the carbon-enriched residual austenite</td>
</tr>
<tr>
<td>(a_{\alpha}, c_{\alpha})</td>
<td>Lattice parameters of tetragonal martensite</td>
</tr>
<tr>
<td>(B_s)</td>
<td>Bainite–start temperature</td>
</tr>
<tr>
<td>(f)</td>
<td>Fraction of austenite transformed to martensite</td>
</tr>
<tr>
<td>(M_S)</td>
<td>Martensite–start temperature</td>
</tr>
<tr>
<td>(M_F)</td>
<td>Martensite–finish temperature</td>
</tr>
<tr>
<td>(N_i)</td>
<td>Number of original nucleation sites for martensite per unit volume of sample</td>
</tr>
<tr>
<td>(N)</td>
<td>Number of new martensite plates per unit volume of austenite</td>
</tr>
<tr>
<td>(N_v)</td>
<td>Number of new martensite plates per unit volume of sample</td>
</tr>
<tr>
<td>(T_B)</td>
<td>Temperature at which sample is transformed to bainitic ferrite and carbon enriched residual austenite</td>
</tr>
<tr>
<td>(T_Q)</td>
<td>Temperature to which the sample is cooled below (M_S)</td>
</tr>
<tr>
<td>(\Delta G^{\gamma\alpha'})</td>
<td>Driving force for diffusionless transformation</td>
</tr>
<tr>
<td>(\bar{V})</td>
<td>Average volume per newly formed plate</td>
</tr>
<tr>
<td>(V_{\alpha'})</td>
<td>Absolute volume fraction of martensite</td>
</tr>
<tr>
<td>(V_\gamma)</td>
<td>Volume fraction of austenite present in the sample prior to martensitic transformation</td>
</tr>
<tr>
<td>(V_{\gamma_r})</td>
<td>Volume fraction of austenite retained at room temperature</td>
</tr>
<tr>
<td>(V_{\alpha_b})</td>
<td>Volume fraction of bainitic ferrite</td>
</tr>
</tbody>
</table>
5.1 Introduction

Mixed microstructures consisting of bainite and martensite are usually a consequence of inadequate heat-treatment or the use of steels with insufficient martensite-hardenability in applications involving heavy sections. Early research [1-3] suggested that the presence of bainite in an otherwise martensitic microstructure generally leads to a deterioration in ductility, toughness and strength.

Contrary to these generally pessimistic indications of the properties of mixed microstructures, more recent work by Tomita and Okabayashi[4,5] has tended to indicate that in some circumstances, the presence of bainite in a predominantly martensitic microstructure enhances both strength and toughness relative to the single phase samples. They explained their results by postulating that as the lower bainite subdivides regions of austenite, there is in effect a refinement of the austenite grain size and consequently a refinement of the martensite packet size on the subsequent transformation of austenite. This leads to a strengthening of the martensite via a grain size effect. In addition, the strength of the bainite is supposed to be enhanced by the constraint provided to its deformation by the stronger martensite.

Thus, mixed microstructures of bainite and martensite are bound to become more prominent commercially, but are also of interest from a fundamental point of view, to reveal the influence of partial bainitic reaction on the subsequent formation of martensite. An attempt is therefore made here to model the development of martensitic transformation in a high-silicon, medium carbon steel, with the commercial designation “300M”, with the particular aim of rationalising the formation of martensite in samples which already contain some bainitic ferrite. For this reason, some of the samples studied were quenched directly from the austenitisation temperature, while others were first transformed isothermally to bainitic ferrite, before cooling to ambient temperature to allow some of the residual austenite to decompose to martensite. The studies were carried out both on chemically segregated, “as-received” samples, and for comparison purposes, on samples homogenised by prolonged heat-treatment at a high temperature.

The work presented here extends earlier research [6,7], which focused on the development of the bainite reaction, to the modelling of the subsequent transformation of some of the residual austenite into martensite. The ultimate aim of this research
program is to develop phase transformation theory which will permit the prediction of microstructural evolution in commercial steels which contain high silicon concentrations. Such steels have a demonstrated potential as far as good combinations of strength and toughness are concerned [8–12]. Commercial steels are usually chemically heterogeneous, and such segregation is known [13–21] to cause significant changes in the kinetics and thermodynamics of the phase transformations; it was also intended to investigate the effect of the segregation on martensitic transformation.

5.2 Dilatometry

The dilatometric specimens were quenched to room temperature after an appropriately long time at the isothermal temperatures $T_B$ (until the bainite reaction ceased), for a variety of temperatures below the bainite–start temperature ($B_s$). Dilatometric curves showing the relative length change due to transformation as a function of temperature are shown in Fig. 5.1

In these curves, any deviation from a straight line as the specimen cools represents the onset of martensitic transformation, so that a martensitic–start temperature ($M_s$) can be determined. This relies on the experimental observation that the austenite in the 300M steel used has a constant thermal expansivity over the temperature range of interest [6,7]. The expansion that occurs when austenite transforms to martensite is then detected as the deviation described earlier.

As expected, a higher martensite–start temperature was observed when the sample had been transformed partially to bainite at a higher temperature ($T_B$), since a lower maximum volume fraction of bainite is obtained as $T_B$ is raised. It is also evident that the $M_s$ temperature of the residual austenite* is higher for heterogeneous specimens when compared with the chemically homogeneous samples (Fig. 5.2). This is consistent with the fact that relatively less bainite forms in heterogeneous samples, so that the residual austenite then contains a lower carbon concentration relative to homogeneous specimens heat–treated in an identical manner [7]. As a result, the tendency to form martensite is more pronounced in heterogeneous samples. This is also reflected in the

* The term “residual austenite” refers to that which exists at the reaction temperature during isothermal transformation to bainite. “Retained austenite” refers to the austenite which remains untransformed after cooling the specimen to ambient temperature.
calculated data presented in Fig. 5.2, since for identical transformation conditions, it is established that more bainitic ferrite can be obtained in the homogeneous samples, giving a higher degree of carbon-enrichment in the residual austenite in those samples, and hence lowering the martensite-start temperature of the residual austenite. The carbon concentration of the residual austenite \( (x_\gamma) \) was calculated from the volume fraction of bainite, assuming a homogeneous distribution of carbon in austenite.

\[
x_\gamma \simeq \bar{x} + \frac{V_{ab}(\bar{x} - x_a)}{1 - V_{ab}}.
\]  

(5.1)

where \( \bar{x} \) is the average carbon concentration of the alloy and \( x_a \) is the carbon concentration of the bainitic ferrite. Since the latter is always rather small when compared with \( \bar{x} \), it is assumed here to be given by the carbon concentration of ferrite which is in equilibrium with austenite in a Fe–C alloy, as calculated\(^{[22]}\) using the McLellan and Dunn quasichemical thermodynamic model\(^{[23]}\).

The calculations assume a homogeneous distribution of carbon in the residual austenite, and hence underestimate the martensite–start temperature (Fig. 5.2). The real distribution of carbon is known to be inhomogeneous following bainitic ferrite growth\(^{[24–27]}\), so that the relatively dilute regions will tend to transform martensitically at higher temperature. Consistent with this, the degree of underestimation is found to decrease as the volume fraction of bainitic ferrite decreases \( (i.e., \, T_B \text{ increases}) \). Observation of occasional pockets of twinned martensite through electron microscopy confirms the presence of high carbon regions (Fig. 5.3).

As a check on the \( M_S \) calculations, a homogeneised sample was quenched directly to ambient temperature; a martensite–start temperature \( (M_S) \) of 280 °C was observed, and this agrees reasonably with the thermodynamically calculated\(^{[28,29]}\) \( M_S \) temperature of 276 °C.

As expected, further length changes were observed as the samples were cooled below the \( M_S \) temperature, as more of the residual austenite decomposed martensitically. The relationship between the amount of martensite formed as a function of undercooling below the \( M_S \) temperature was, as expected, found to be nonlinear. The volume fraction of martensite produced at first is small; the extent of transformation as a function of undercooling below \( M_S \) then increases, although it eventually begins to decrease towards zero as the amount of unreacted austenite decreases towards zero, or as the small quantity left untransformed stabilises to further decomposition.
The "martensite-finish temperature" \( (M_F) \) is not a meaningful concept from a fundamental point of view, because the reaction progresses with further and eventually, decreasing increments of volume fraction as the temperature is reduced below \( M_S \), in principle never reaching completion. Small amounts of retained austenite thus remain stable even at very low temperatures. The transformation of the last traces of austenite becomes more and more difficult as the amount of austenite decreases probably due to mechanical stabilisation\(^{30,31} \) (Fig. 5.1).

The temperature range over which martensite forms is usually a characteristic of the specific alloy composition and particularly, the carbon concentration. The range is generally greater when the residual austenite has a lower carbon content. It can be seen from Fig. 5.1 that the range \( M_S - M_F \) is always greater in the heterogeneous specimens when compared with the homogeneous samples, especially for low values of \( T_B \). This is to be expected since each of the heterogeneous samples in effect consists of a composite of different alloys, each of which will have its own transformation range. The superposition of these ranges should consequently give a larger overall value of \( (M_S - M_F) \) when compared with the homogeneous samples. Figure 5.1 shows that martensite formation starts at lower temperatures in the homogeneous samples and reaches apparent "completion" sooner than the corresponding heterogeneous samples.

\textit{5.2.1 Calculation of Volume Fraction}

Dilatometric data in the form of the relative length change \( \Delta L/L \) (where \( L \) is the length of the sample at ambient temperature, and \( \Delta L \) is the change in length due to transformation) were converted into the fraction \( (f) \) of austenite which is transformed to martensite using the following relationship:

\[
f = \frac{3\Delta L a_{\gamma}^3}{V_\gamma L(2a_{\alpha}^2c_{\alpha} - a_{\gamma}^2)}
\]  \hspace{1cm} (5.2)

where \( a_{\gamma} \) is the lattice parameter of the the carbon-enriched residual austenite, \( a_\alpha \) and \( c_\alpha \) are the lattice parameters of tetragonal martensite, and \( V_\gamma \) is the volume fraction of austenite present in the sample prior to martensitic transformation. The absolute volume fraction of martensite \( (V_{\alpha'}) \) can be obtained by multiplying the fraction of austenite transformed to martensite \( (f) \) with the actual volume fraction of austenite \( (V_\gamma) \) initially present at \( T_B \), i.e.,

\[
V_{\alpha'} = fV_\gamma
\]  \hspace{1cm} (5.3)
A computer program was written and used for these calculations. The program takes full account of the changes in lattice parameters as a function of alloy composition and temperature, as described elsewhere [7,32]. Figure 5.4 shows the volume fractions of martensite, obtained for homogeneous and heterogeneous specimens after the specimens had been transformed isothermally to bainite at the temperatures indicated, with enough time at the isothermal transformation temperatures to ensure the cessation of bainite formation.

There is a rapid increase in the volume fraction of martensite \((V_{\alpha'})\) with an increase in the isothermal transformation temperature \(T_B\), which is consistent with the respective measured and calculated \(M_S\) temperature data (Fig. 5.2).

### 5.2.2 Retained Austenite

Given that the volume fractions of bainite and martensite were determined by dilatometry, it is relatively easy to calculate the volume fraction of austenite retained \((V_\gamma)\) at room temperature by difference:

\[
V_\gamma = 1 - V_{\alpha} - V_{\alpha'}
\]  

(5.4)

It was found that for both the homogeneous and heterogeneous specimens, the volume fraction of retained austenite decreased at first, and then increased with the isothermal transformation temperature \(T_B\). At \(T_B = 400\) °C, a relatively larger quantity of retained austenite was obtained for the homogeneous specimen (Fig. 5.5).

It is to be noted (Fig. 5.5) that in previous experiments, a relatively higher volume fraction of bainite was obtained in the case of the homogeneous specimen relative to the heterogeneous sample transformed at 400 °C. This means that more film austenite\(^*\) can be expected than the blocky morphology after the formation of bainite in homogeneous sample. This film austenite, since it is trapped in the immediate vicinity of bainite subunits, is known to contain a higher carbon content than the blocky austenite\[^{33,34}\] and is difficult to transform to martensite. There is as a result, a sudden rise in the volume fraction of austenite retained for the samples transformed to bainite at 400 °C.

\(^*\) Film austenite is that retained between the subunits within a given sheaf of bainite while "blocky austenite" is the retained austenite, exhibiting a triangular shape in two dimensional sections, bounded by different crystallographic variants of bainite sheaves [8,9].
This also explains the marked drop in the volume fraction of martensite ($V_{\alpha'}$) (Fig. 5.4). An increase in the calculated volume fraction of retained austenite with an increase in isothermal transformation temperature results as higher amount of residual austenite with lower carbon content is being produced.

### 5.2.9 Instability of Residual Austenite

A parameter representing the stability of residual austenite can be defined by the ratio of volume fraction of martensite to the volume fraction of residual austenite at the isothermal bainite transformation temperature \cite{8,9}, i.e., $\frac{V_{\alpha'}}{(1-V_{\alpha'})}$. Figure 5.6 shows a plot of the stability parameter as a function of carbon content of residual austenite ($x_\gamma$) for the homogeneous and heterogeneous specimens.

The instability of residual austenite at any isothermal transformation temperature is higher for the heterogeneous material presumably because in all cases, the degree of reaction to bainite was lower than in comparative homogeneous samples. As has been noted previously \cite{8,9}, the observations also indicate that the enhanced stability arises from the finely divided state of the bainitic residual austenite whose carbon content is usually higher when compared with the rest of the austenite. The differences in instabilities between homogeneous and heterogeneous specimens increase with increases in the maximum degree of bainitic transformation (i.e., with decrease in transformation temperature). It is interesting to note that the bainitic residual austenite becomes increasingly stable as the degree of transformation of bainitic ferrite becomes greater. The films of retained austenite separating the bainitic lenticular plates lead to high strength and they additionally break up the path of propagating cracks since the crack not only has to traverse interphase interfaces and varying crystal structures but its motion can also be dampened by transformation at the crack tip\cite{35}.

### 5.3 Kinetics of Athermal Martensitic Transformation

Any assessment of the overall kinetics of transformations which are thermodynamically of first order in the Ehrenfest classification scheme, must include a consideration of both the nucleation and growth rates of the product phase. On the other hand, for martensitic transformation in steels, the growth rate of the plates can be very high, often limited by the speed of sound in the steel. Furthermore, because of the displacive character of the transformation, the martensite grows in the form of thin plates whose
aspect ratio may be determined by the minimisation of strain energy if the plates are elastically accommodated. Since the coordinated movement of atoms characteristic of displacive reactions cannot in general be sustained across austenite grains which are in different crystallographic orientations, the maximum dimension of each plate must in some way be limited by the austenite grain size. Considering all these factors together, it may as a first approximation be assumed that the volume of material transformed by each plate or lath of martensite is a constant value $V$. In these circumstances, the growth part of the overall kinetics may be neglected, since each nucleus will transform $V$ of the parent phase.

It has been known for a long time[36], that the progress of the athermal martensitic transformation in a sample which is initially fully austenitic, can be described empirically by an equation of the form:

$$1 - f = \exp\{-C_1(M_S - T_Q)\}$$  \hspace{1cm} (5.5)

where $f$ is the volume fraction of martensite divided by the volume fraction of austenite prior to the formation of martensite, $T_Q$ is a temperature to which the sample is cooled below $M_S$; $C_1$ is a constant obtained originally [36] by fitting to experimental data.

Magee[37] demonstrated that this relationship can be justified theoretically if it is assumed that the number of new plates of martensite that form per unit volume of austenite (i.e., $dN$) due to the lowering of temperature below $M_S$ is a positive proportional to the consequential change in the driving force $\Delta G^\gamma$ for diffusionless transformation:

$$dN = -C_2 d(\Delta G^\gamma)$$  \hspace{1cm} (5.6)

where $C_2$ is a proportionality constant. Note that $\Delta G^\gamma$ is given by $G^\gamma - G^\alpha$, where $G^\alpha$ and $G^\gamma$ refer to the Gibbs free energies of unit volumes of martensite and austenite respectively. The change in the volume fraction of martensite is therefore given by:

$$df = \bar{V} dN_V$$  \hspace{1cm} (5.7)

where $dN_V$ is the change in the number of new plates of martensite formed per unit volume of sample, with $dN_V = (1 - f)dN$ and $\bar{V}$ is the average volume per newly formed plate. On combining equations 5.6 & 5.7, and substituting $[d(\Delta G^\gamma)/dT]dT$ for $d(\Delta G^\gamma)$, Magee showed that

$$df = -\bar{V}(1 - f)C_2 [d(\Delta G^\gamma)/dT]dT$$

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which on integration between the limits $M_S$ and $T_Q$ gives

$$\ln\{1 - f\} = \overline{V} C_2 \left[ d(\Delta G^{\gamma_0^*})/dT \right] (M_S - T_Q)$$

or

$$1 - f = \exp\left\{ \overline{V} C_2 \left[ d(\Delta G^{\gamma_0^*})/dT \right] (M_S - T_Q) \right\}. \quad (5.8)$$

The integration procedure used above assumes that the term $[d(\Delta G^{\gamma_0^*})/dT]$ is constant with temperature. The form of the above equation is similar to that of the empirical relation used by Koistinen and Marburger$^{[36]}$, so that

$$C_1 = -\overline{V} C_2 \left[ d(\Delta G^{\gamma_0^*})/dT \right]. \quad (5.9)$$

Graphs illustrating the variation of $\Delta G^{\gamma_0^*}$ as a function of undercooling below $M_S$ are illustrated in Fig. 5.7; they show that it is a good approximation to assume that the variation is linear so that $C_1$ should be approximately constant over the range of interest.

Data are presented in Fig. 5.7 for 300M steel containing a range of carbon concentrations, to simulate martensitic decomposition following partial transformation to bainite. The formation of bainite leads to an enrichment of carbon in the residual austenite. The calculations use the thermodynamic theory and data detailed in references $^{[38,39]}$.

5.3.1 Results of Kinetic Analysis

An attempt was made to fit the data from dilatometric experiments to an empirical equation of the form:

$$1 - f = \exp\{ -C_1(M_S - T_Q) \} \quad (5.10)$$

Graphs of $(M_S - T_Q)$ versus $\ln(1 - f)$ are shown in the Fig. 5.8. Comparison of the as-received heterogenic and the homogenised samples revealed no obvious or systematic differences in the plots (Fig. 5.8). Results of the regression analysis, in which a line passing through the origin was best fitted to the data in each case, are given in the Table 5.1.

The data, when plotted according to equation 5.8 were usually found to deviate from linearity at the very early stages of reaction (Fig. 5.9). It was considered that this failure of the theory may be a consequence of the act that it neglects the autocatalysis
effect. When plates of martensite form, they induce new embryos which are then available for further transformation, this is autocatalysis. Even Magee's interpretation (equations 5.6–5.8) does not explicitly include the autocatalysis factor, although he clearly recognised and discussed the implications of autocatalytic nucleation. Table 5.1 also shows that while the data corresponding to each isothermal transformation temperature, can be correlated well using equation 5.7, the values of $C_1$ calculated from the regression analysis vary significantly when all the experimental data are considered together, again emphasising the failure of the model. It is nevertheless found (Fig. 5.9) that the volume fraction of martensite at ambient temperature as predicted by an empirical application of Koistinen and Marburger's equation is in good agreement with the experimental results, provided that a suitable value of the constant $C_1$ is used. However, the need to use a different value of $C_1$ in each case makes the procedure of little use for predictive purposes.

5.3.2 The Role of Autocatalysis

As pointed out earlier, the model discussed above does not include the effects of autocatalysis. The nucleation of martensite is believed to begin at structural imperfections in the parent phase, such as arrays of dislocations. These are the preexisting defects which, on cooling below the $M_S$ temperature dissociate into suitable partial dislocations in a way which leads to the operational nucleation of martensite\[^{40}\]. The defects are not identical (they vary in potency) and are stimulated to grow into plates of martensite at different degrees of undercooling below the $M_S$ temperature. Thus the volume fraction of martensite, in general, varies only with the degree of undercooling below $M_S$.

Detailed analysis reveals\[^{40–42}\] that the initial number density of preexisting defects typically found in austenite is not large enough to explain the kinetics of martensitic transformation. The extra defects necessary to account for the faster than expected transformation rates are attributed to autocatalysis: when plates of martensite form, they induce new embryos which are then available for further transformation. It has been proposed that the number of autocatalytic sites generated per unit volume at different temperatures can be calculated by integrating the following equation\[^{43}\]:

$$dN = dN_i + d(f'p)$$

(5.11)
where $N_i$ is the number of original nucleation sites per unit volume of sample, which remain after the formation of some martensite, and is given\cite{37} by

$$N_i = (1 - f')N_i^0$$

where $N_i^0$ is the number of original nucleation sites per unit volume of austenite. The term $p$ represents the number of autocatalytic sites generated per unit volume of sample. We assume here that this autocatalytic factor is related linearly to the volume fraction of martensite and hence to $f'$,

$$p = C_3 + C_4 f'$$

(5.12)

then it follows that

$$dN = (-N_i^0 + C_3 + 2C_4 f') df'.$$

(5.13)

Since $\bar{V}$ is assumed to be constant in the present analysis, $df'/\bar{V} = (1 - f') dN$ so that

$$\int_0^f \frac{df'}{\bar{V}(1 - f')} = \int_0^f (-N_i^0 + C_3 + 2C_4 f') df'.$$

(5.14)

On carrying out the integration, we get

$$p = N_i^0 - \frac{\ln\{1 - f\}}{f\bar{V}}.$$  

(5.15)

It is noteworthy that as $f \to 0$, $p \to N_i^0 + \frac{1}{\bar{V}}$.

A value of $\bar{V}$ can be estimated to be $\sim 20 \mu\text{m}^3$, on the basis that a typical plate of martensite will have the approximate dimensions $0.2 \times 10 \times 10 \mu\text{m}$. With this assumed value, and the experimentally measured volume fractions of martensite, calculated values of $p - N_i^0$ were plotted against $M_S - T_Q$, as illustrated in Fig. 5.10.

It is evident that the relationship between these variables is approximately linear, and may be expressed as follows:

$$p - N_i^0 = C_5 + C_6 (M_S - T_Q)$$

(5.16)

where $C_5$ and $C_6$ are constants defining the best fit line between the variables. On setting $M - T_Q = 0$, or in other words, $f = 0$, it is found that $p \to N_i^0 + \frac{1}{\bar{V}}$ so that

$$C_5 = \frac{1}{\bar{V}}.$$
so that

$$p - N_i^0 = \frac{1}{V} + C_6(M_S - T_Q).$$  \hspace{1cm} (5.17)$$

On combining this relationship with equations 5.13, it follows that

$$\frac{-\ln\{1 - f\}}{f} = 1 + \bar{V}C_6(M_S - T_Q)$$  \hspace{1cm} (5.18)

or

$$\frac{-\ln\{1 - f\}}{f} = 1 + C_7(M_S - T_Q)$$  \hspace{1cm} (5.19)

where $C_7 = \bar{V}C_6$. This equation represents a new law for the development of martensitic transformation as a function of undercooling below the $M_S$ temperature. Its application is considered below. It should be noted that in the analysis, homogeneous and heterogeneous samples are treated alike as previously no remarkable difference was observed in the development of martensite reaction in the two kinds of samples.

The experimental data as fitted to the above equation are represented in Fig. 5.11. A better correlation was obtained when compared with the previous model based on equation 5.8.

Figure 5.12 shows that the new model can accurately predict the kinetics of the martensite reaction at all stages. As the data include directly-quenched samples as well as those partially transformed to bainite and quenched from this isothermal transformation temperature, it can be concluded further that the defects generated by bainitic transformation do not give rise to a large amount of autocatalytic nucleation of martensite.

5.3.3 Variation of $V$ with Undercooling

Even with the new model developed above, it was assumed that $V$ is constant during the course of the reaction. Fisher's model\textsuperscript{[44-46]} for plate martensite predicts that the average volume of martensite plates decreases strongly as the transformation proceeds. The theory assumes that the transformation is random throughout a specimen and that the plates partition the $\gamma$-grains into smaller compartments. As a result, the later forming plates should tend to be smaller. However, the nucleation of martensite may not be random throughout\textsuperscript{[47]}, as most martensite plates nucleate in the vicinity of other martensite plates due to the autocatalysis effect. It has been recognised\textsuperscript{[37]} that the first observable transformation is due to several clusters of plates rather than a random distribution of plates.
Magee et al. [48] have shown experimentally that for Fe-23.8Ni-0.42C wt.% and Fe-28.5Ni-0.40C wt.% alloys, there is no sensible decrease in $V$ at volume fractions up to 0.55. However, at high volume fractions, the geometrical partitioning effect is expected to be important, and $V$ will be expected to decrease as volume fraction increases. Guimarães et al. [49] used Fullman’s stereographic method [50] to determine both the mean plate radius, $r$, and volume $V$. The mean plate thickness was estimated through the equation proposed by Chen and Winchell [51]:

$$\bar{t} = \frac{V_{\alpha'}}{S_v}$$

(5.20)

where $(V_{\alpha'})$ is the volume fraction of martensite and $S_v$ the mean density of martensite midplane in the material. The calculated aspect ratio $\bar{t}/\bar{r}$ was found to reach a maximum at some intermediate fraction transformed. Guimarães [52], investigating the influence of austenite grain sizes on the mean volume of martensite plates in Fe-31.9Ni-0.02C wt.%, found that $V$ is constant in materials with finer austenite grain size, but it noticeably decreases as the fraction transformed increases in samples with coarser austenite grain sizes. In the later case, the Fisher’s partitioning effect is probably more important when compared with the situation for fine austenite grain structures. His computer modelling shows that a fine grain size favours the formation of clusters of partially transformed grains and also enhances autocatalysis in the grains, so that $V$ is not sensitive to the volume fraction transformed.

In the present model particularly good agreement has been observed between calculated and experimental volume fractions of martensite, although it slightly overestimates at low fractions transformed. That may be due to the fact that the model assumes a constant value of $V$ at all stages of transformation. Moreover, the model assumes that all nucleation sites have the same activation energy. Magee [53] showed that there is a distribution of effectiveness of nucleation sites. These approximations require much further research and characterisation.

5.4 Conclusions

The development of martensitic transformation has been studied using dilatometry, from both a fully austenitic starting microstructure and from a microstructure

* Geometrical partitioning is based on the observation that the initial martensite plates divide the sample into progressively smaller compartments.

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containing a mixture of upper bainitic ferrite and carbon–enriched austenite. It is found that the presence of bainitic ferrite does not significantly alter the way in which the subsequent transformation to martensite occurs. In fact all the data can be rationalised using a new model of athermal martensite kinetics, which includes an effect of autocatalytic nucleation, subject to the approximation that all that plates of martensite have identical volume.

For the levels of chemical segregation observed in the steel studied, the major effect on martensitic transformation is to extend the range over which the reaction occurs relative to homogenised samples. Otherwise, the same parameters can be used to predict martensitic reaction in all samples, within the limits of experimental error.
Fig. 5.1: Dilatometric curves showing the transformation to martensite in heterogeneous and homogeneous steels, after the specimens were isothermally transformed to bainite at different temperatures, with enough time at each isothermal transformation temperature to ensure that bainitic ferrite formation stopped. Graphs (a), (c), (e), (g) and (i) are for homogeneous samples and (b), (d), (f), (h) and (j) are from heterogeneous samples.
Fig. 5.1: (continued....)
Fig. 5.2: Thermodynamically calculated\textsuperscript{[27,28]} and experimentally determined $M_S$ temperatures for homogenised and heterogeneous samples, after partial isothermal transformation to bainite.
Fig. 5.3: Transmission electron micrographs showing twinned martensite in a homogenised 300M steel specimen which is isothermally transformed to bainite at 420 °C before quenching to room temperature, (a) bright field image, (b) dark field image, (c) untwinned martensite.
Fig. 5.4: Volume fraction of martensite obtained for homogeneous and heterogeneous specimens. The specimens were transformed initially to bainite at different isothermal temperatures, as indicated in the diagram. Hence, in each case the residual austenite, i.e., left after transformation to bainite, had a different carbon concentration which decreases as the bainite transformation temperature increases.

Fig. 5.5: Volume fraction of austenite retained obtained by difference and experimental volume fraction of bainite, in samples partially transformed to bainite followed by quenching to room temperature.
Fig. 5.6: Variation of the instability of the residual austenite which is left untransformed after the bainite reaction stops, with its carbon content.

Fig. 5.7: Plots of $\Delta G^\gamma/\alpha$ versus $M_S - T_Q$ for 300M steel containing a variety of carbon concentrations (wt.%).
Fig. 5.8: Results of the regression analysis of the experimental data fitted to Koistinen and Marburger's empirical equation.
<table>
<thead>
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<th>Heterogeneous</th>
</tr>
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</tr>
<tr>
<td>Directly Quenched</td>
<td>-0.98</td>
<td>-0.0055</td>
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Table 5.1: *Regression constants for the curves shown in Fig. 5.8.*
Fig. 5.9: Comparison of the observed and calculated volume fractions of martensite. The calculations utilise the Koistinen and Marburger's equation. A common value of 0.004 was assigned to $C_1$ for all these calculations. The true volume fraction of martensite (a) at 20 °C only and (b) at all temperatures where measurements were made.
Fig. 5.10: Graphs illustrating the linear relationship between $(p - N_i^0)$ and $(M_S - T_Q)$. 

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Fig. 5.11: Results of the regression analysis as the experimental data were fitted to an equation of the form \[-1 + \ln(1-f) = C_f(M_S - T_q).\]

Fig. 5.12: Comparison of experimental results with those calculated by the new model based on equation 5.18.
REFERENCES

Chapter 6
REAUSTENITISATION IN HETEROGENEOUS STEELS

6.1 Introduction

There has been a lot of research on the decomposition of austenite but the same is far from true for the reverse transformation, i.e., the formation of austenite during the heating of steels. In the heat-affected zone of a multirun weld, the layers deposited initially are reheated by the deposition of subsequent layers and consequently may experience complicated thermal cycles which result in several modifications of the initial microstructure. It is necessary to understand the variety of stages of annealing and reaustenitisation to be able to calculate the microstructure of the heat affected zones of such welds. The situation is in fact even more complex, as the material being annealed and reaustenitised in a multirun weld is usually chemically heterogeneous since the welds almost always solidify under nonequilibrium conditions.

The reaustenitisation process under industrial conditions (and indeed, for all reported studies) is known to depend on the details of the corresponding nucleation and growth process. The nucleation site, growth rate and austenite morphologies depend strongly on the initial microstructure of the steel. Once the reverse transformation is complete, the austenite thus produced coarsens, reducing its total grain boundary energy per unit volume. The rate of grain coarsening is in general known to depend on the alloy chemistry, the temperature and on the amount of grain surface per unit volume of sample. The maximum grain size thus obtained again depends on the composition and the annealing temperature, although normal grain growth usually becomes impossible before a metal has become converted into a single crystal. When dispersed particles are present in the material, a limiting grain size exists, beyond which grains cease to grow. The limiting size is determined approximately by the ratio of the mean radius and volume fraction of the particles. Hence, the ultimate austenite grain diameter will be determined by both the reverse transformation kinetics, and any grain growth which occurs after the completion of the transformation. The whole subject of austenite formation is fascinating and complicated by the awesome variety
of starting microstructures which can be heated into the austenite+ferrite phase field. This work is limited to isothermal reaustenitisation experiments in which the starting microstructure consists of a two-phase mixture of bainitic ferrite and residual austenite.

6.2 Isothermal Reaustenitisation

Isothermal reaustenitisation experiments were carried out on the as-received (heterogeneous) specimens, austenitised at 950 °C for 10 minutes, and then isothermally transformed to bainite at $T_B = 320$ °C and $T_B = 400$ °C for approximately 45 minutes in each case. Fig. 6.1 illustrates the heat-treatment schematically. The period of 45 minutes is long enough to permit the formation of bainitic ferrite to cease (Fig. 6.2). After completion of the isothermal heat treatment at $T_B$, the samples were heated rapidly to a temperature $T_\gamma$ to promote the growth of austenite. It has already been shown (Fig. 6.3) that for the alloy used, the bainitic reaction terminates when the carbon concentration of the residual austenite, $x_\gamma$, reaches the concentration given by the $T_0$ curve on the phase diagram. The relatively high silicon content of the alloy helps to retard the precipitation of cementite\textsuperscript{[10-15]} from austenite and the microstructure then contains only bainitic ferrite and carbon enriched residual austenite at the isothermal transformation temperature ($T_B$). The carbon of residual austenite, $x_\gamma$, can be determined readily from a simple mass balance procedure\textsuperscript{[16]}. Furthermore, the lack of any reactions other than the growth of bainitic ferrite makes the interpretation of data easier, since the overlap of reactions does not have to be taken into account. Although bainitic transformation at $T_B$ ceases before all the austenite is consumed, the composition of austenite is still far from equilibrium. Hence, although it is unable to decompose further to bainite, it can, given sufficient time, decompose by reconstructive transformation into more ferrite and carbides\textsuperscript{[17]}. At the temperatures where bainite forms, this secondary reaction can be extremely sluggish, but it was found that when the samples were heated from $T_B$ towards $T_\gamma$ at slow heating rates (Fig. 6.4), the residual austenite tended to decompose during heating to pearlite\textsuperscript{*} and to mixture of ferrite and discrete carbides. This decomposition during heating could be avoided by utilising a faster heating rate, as illustrated in Fig. 6.4. Consequently, for all other experiments, heating rate of 100 °C s\textsuperscript{-1} were used for the temperature range $T_B - T_\gamma$.

\textsuperscript{*} Metallographic evidence for decomposition to pearlite during heating cannot be shown as the sample is then completely reaustenitised at $T_\gamma = 770$ °C.
The results obtained using dilatometry are shown in Figs. 6.5 and 6.6. It is evident that there is no decomposition of austenite during heating from $T_B$ to $T_\gamma$. It is important to note that the specimens were not cooled below $T_B$ prior to heating to elevated temperatures, in order to avoid any martensitic decomposition of the residual austenite left after the formation of bainite stops. Thus, when the mixed microstructure of just bainitic ferrite and carbon-enriched residual austenite is heated rapidly to $T_\gamma$, the nucleation of new austenite becomes unnecessary and the growth process can be studied in isolation\cite{18}.

During attempts to carry out isothermal reaustenitisation experiments at very high temperatures (greater than about 770 $^\circ$C), it was found impossible, using the equipment available, to avoid a small degree of austenite formation just before the isothermal reaction temperature $T_\gamma$ was reached. Hence the data for $T_\gamma$ were corrected to take this prior austenite formation into account, using the procedure given in reference \cite{19} and is illustrated in Fig. 6.7. If there is no transformation during heating, the length of the specimen should vary linearly with temperature due to the constant thermal expansion coefficients for the phases involved in this study and over the temperature range of interest, as illustrated in Fig. 6.7a. In that case, the maximum relative length change due to austenite growth can be measured directly as the difference between points ‘a’ and ‘b’. Note that curve remains linear until the designated $T_\gamma$ is reached, indicating no change in microstructure before the sample reaches $T_\gamma$. The other typical case is shown in Fig. 6.7b, where because of the high value of $T_\gamma$ where the kinetics are rapid, reaustenitisation starts during heating in spite of high heating rate used. Therefore, the deviation from the straight line corresponding to the linear thermal expansion of the specimen as extrapolated from low temperatures can be attributed to the growth of austenite which has occurred during heating to $T_\gamma$. If the low temperature part of the curve is extrapolated to the reaction temperature, the vertical difference between the extrapolated line and the actual length change curve gives the true length change due to transformation at $T_\gamma$, as if no reaction had occurred during heating to isothermal reaustenitisation temperature. The distance $a-a'$ is therefore added to $a'-b$ to correct for prior reaction.
6.3 Results and Discussion

In all the cases transformation rate was rapid at first, but decreased with time until eventually the rate became undetectable. The rate of this reverse transformation to austenite was found to increase monotonically as $T_\gamma$ was raised. This is because, unlike the transformation of austenite to ferrite, both the diffusion coefficient and driving force increase with superheating. The maximum extent of austenite formation, as deduced from the maximum relative length change (Fig. 6.8), also increases with increasing reaustenitisation temperature, from a volume of zero at the temperature where the carbon concentration of the residual austenite equals that given by $A_{\gamma 3}$ curve of the phase diagram, as predicted by Yang and Bhadeshia\cite{18}. It is particularly interesting that the growth of austenite does not begin immediately the temperature is raised above $T_B$. This is a direct consequence of the incomplete-reaction phenomenon associated with bainitic reaction, in which the reaction stops prematurely before the austenite achieves its equilibrium composition. Hence austenite growth cannot begin until a much higher temperature is reached, giving a large hysteresis between the forward and reverse reactions.

It is interesting to note that there is not much of a difference in the maximum relative length change for the samples transformed initially to bainite at 320 °C and those transformed at 400 °C, for low values of $T_\gamma$. But this difference becomes quite significant at $T_\gamma=760$ °C (Fig. 6.8) when both types of samples transform completely to austenite. This is due to the fact that the starting microstructure of the samples transformed to bainite at 400 °C prior to reaustenitisation contains a higher volume fraction of residual austenite compared with those initially transformed to bainite at 320 °C. The differences are clear from the representative micrographs of the two cases shown in Fig. 6.9. Those specimens were quenched down to room temperature after transformation to bainite almost ceased; the carbon enriched austenite has to some extent transformed to martensite. For any given isothermal reaustenitisation temperature $T_\gamma$, the extent of austenite growth is larger for lower $T_B$. This expected since the driving force for austenite growth is larger at any $T_\gamma$ if its carbon concentration is larger when compared with the average concentration $\bar{x}$, i.e., as $T_B$ is reduced. Another way of looking at this is to realise that for lower $T_B$, there exists a larger volume fraction of bainitic ferrite which can transform back to austenite on superheating.
Any qualitative comparison of the volume fractions of austenite obtained in homogeneous and heterogeneous specimens must be carried out bearing in mind that the two kinds of samples do not have equivalent starting microstructures. The extent of bainitic transformation at $T_B$ is different for the two cases (Table 6.1) so that the residual austenite in the two cases is expected to contain different carbon contents even if the transformation conditions are otherwise identical. Micrographs of partially reaustenitised homogeneous and heterogeneous specimens are shown in Fig. 6.10. Austenite formation is found to occur more uniformly in the homogeneous sample, whereas for the heterogeneous specimens the transformation is more dominant in the solute-enriched bands. It can be seen more clearly in Fig. 6.11.

These bands, being the last to transform to bainite, are expected to have most of the carbon rejected from the neighbouring transformed (bainitic ferrite) areas and as a result will have lower $A_{e3}$ temperatures relative to the remainder of the sample. In most cases reaustenitisation seems to proceed by the “erosion” of the bainitic ferrite without any evidence of the independent nucleation of austenite.

All the reaustenitised (heterogeneous) specimens were helium-gas quenched from $T_γ$ to ambient temperature. Dilatometric curves of the relative length change as a function of temperature for that part of the thermal cycle are presented in Figs. 6.12 and 6.13. In each diagram, any deviation from a straight line during the cooling of the specimen represents the onset of martensitic transformation, so that a martensitic-start temperature ($M_s$) of any austenite can be determined.

It is clear from Figs. 6.14a and 6.15a that the experimentally measured $M_s$ temperatures of the new austenite increases with increasing reaustenitisation temperature for the specimen initially transformed to bainite at $T_B = 320$ °C. This is exactly as expected since the carbon concentration decreases and volume fraction of the austenite that forms increases as $T_γ$ is raised. However, in case of the specimens initially transformed at $T_B = 400$ °C, the $M_s$ temperature was found to decrease with an increase in $T_γ$ in the small temperature range considered.
A relationship between the carbon concentration of any austenite and its thermodynamically calculated martensitic-start temperature was deduced by best fitting a curve to the data (Fig. 6.16) for this particular alloy. The empirical equation thus obtained is found to be

$$x_\gamma = \frac{496 - M_s}{490}$$  \hspace{1cm} (6.1)

where $x_\gamma$ is carbon concentration of austenite in weight percent, and $M_s$ is the martensitic-start temperature in degrees centigrade. If $x_\gamma$ is expressed in units of mole fraction, then the equation becomes:

$$x_\gamma = \frac{503 - M_s}{11360}$$  \hspace{1cm} (6.2)

Equation 6.1 was used to calculate the carbon concentration of austenite that forms at $T_\gamma$ from the $M_s$ temperatures measured using dilatometry and the results are shown in Figs. 6.14b and 6.15b.

As expected, Fig. 6.14b shows a decrease in the carbon content of austenite with increasing reaustenitisation temperature for $T_B = 320 \, ^\circ C$. On the other hand, an increase in the carbon content of austenite with increasing $T_\gamma$ is observed in the case $T_B = 400 \, ^\circ C$ as in shown in Fig 6.15b. This unusual behaviour can be explained as follows.

For the samples whose initial microstructure was generated at $T_B = 320 \, ^\circ C$, due to higher driving force for the $\gamma \rightarrow \alpha_b$, the bainitic ferrite (and regions of residual austenite) is distributed uniformly in the solute-depleted as well as in solute-rich regions (Fig. 6.9). Due to homogeneous distribution of the austenite, the specimen behaves, more or less, as a chemically homogeneous sample and the effective $A_{e3}$ curve determining the growth of austenite will be that of a homogeneous alloy. When such a microstructure is reaustenitised the growth of austenite takes place uniformly all over the sample.
At the lower reaustenitisation temperatures, a large amount of carbon is tied-up in a relatively small volume fraction of austenite; as the reaustenitisation temperature is increased, more austenite forms and consequently gets diluted in carbon. The carbon content of austenite for a homogeneous alloy should follow the path ‘d – d’ with increasing reaustenitisation temperature as shown in Fig. 6.17. Hence, we can see, Fig. 6.14a shows an increase in the Ms temperature with increasing reaustenitisation temperature.

But the situation for $T_B = 400 \, ^\circ\text{C}$ is rather different, when most of the austenite in the starting microstructure being confined eventually to substitutional solute-enriched regions (Fig. 6.9). Consequently, the effective $A_{e3}$ curve controlling austenite growth will not be a single curve, but rather a range of $A_{e3}$ curves will be at work. This is represented in Figs. 6.17 and 6.18. At the lower reaustenitisation temperatures, the reaction is much more restricted to solute-enriched regions with the lower $A_{e3}$ temperatures. The growth of austenite will stop at a point ‘c’ on the $A_{e3}$ curve for the solute-enriched regions. With an increase in $T_\gamma$, austenite bands thicken and advance into regions of relatively lower $A_{e3}$ temperature, i.e. the relevant $A_{e3}$ curve moves towards the solute-depleted regions, following the path ‘c – d’ as shown in Figs. 6.17 and 6.18. The growth of austenite will then stop at a point somewhere away from the $A_{e3}$ curve of solute enriched region but near the $A_{e3}$ curve of solute depleted region on the phase diagram. In this way, the carbon concentration of austenite is expected to increase with an increase in $T_\gamma$, as is observed experimentally via the Ms temperatures.

The volume fraction $V_{\gamma s}$ of austenite in a heterogeneous sample transformed at a temperature $T_\gamma$ is given by the lever rule of the phase diagram shown in Fig. 6.17.\[ V_{\gamma s} = \frac{ab}{ac} \] (6.3)

At the same $T_\gamma$, volume fraction $V_{\gamma h}$ of austenite formed in a homogeneous alloy (or in a heterogeneous sample which transforms uniformly to bainite at $T_B$) should be\[ V_{\gamma h} = \frac{ab}{ad} \] (6.4)

As $ac < ad$, hence, $V_{\gamma s} > V_{\gamma h}$ for the samples reaustenitised at the same temperature $T_\gamma$. 

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6.9.1 Experimental Confirmation of the "Yang and Bhadeshia Model"

Yang and Bhadeshia [18] have investigated the growth of austenite from bainitic ferrite in a matrix of austenite in homogeneous steels. Their model explains the variations in the maximum degree of reaustenitisation to be expected as a function of temperature, the reaction start temperature $T_\gamma$, the temperature above which the completion of reaustenitisation occurs, and the equilibrium austenite volume fraction transformed during the isothermal holding as a function of the equilibrium carbon concentration of austenite and the carbon concentration of residual austenite when the isothermal bainite transformation has ceased. Bainite is known to exhibit an incomplete reaction phenomenon [16, 23]; the reaction stops when the carbon concentration of the residual austenite reaches the $T_0$ curve on the phase diagram and in this sense stops prematurely before an equilibrium volume fraction of bainite is obtained. So, the carbon concentration $x_\gamma$ of the residual austenite, when the formation of bainite ceases during isothermal holding at the temperature $T_B$, is given by;

\[ x_\gamma = x_{T_0}\{T_B\} \quad (6.5) \]

Where $x_{T_0}$ is the carbon concentration of the residual austenite at a temperature, where ferrite, whose free energy has been raised by a stored energy term associated with the transformation strain, and austenite of identical composition have the same free energy. The experimental data obtained in the present work for $x_\gamma$ are marked as points 'a' and 'b' on Fig. 6.19, which represent the carbon content of austenite after the specimen were transformed to bainite at $T_B = 320$ °C and $T_B = 400$ °C respectively. In this phase diagram, a set of $T_0$ and $A_{e3}$ phase boundaries has been calculated for the range of chemical compositions detected experimentally. Since the microanalysis technique draws information from an interaction volume which is about $4.5 \mu m^3$, the actual variations in solute concentrations may be underestimated. It should be noted that the values of $x_\gamma$ for cases 'a' and 'b' are much less than the equilibrium carbon concentration ($x_{Ae3}$) at the respective transformation temperatures. Hence, the reverse transformation cannot be expected to happen immediately the temperature is raised above that at which the bainite grows (i.e. $T_B$). The formation of austenite will occur first at a temperature where $x_{T_0} = x_{Ae3}$ for the austenite whose carbon content is given by the points 'c' and 'd' in the Fig. 6.19.

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These temperatures have been marked as $T_{\gamma a}$ and $T_{\gamma b}$ on the $A_{c3}$ phase boundary. The experimental results support the prediction\cite{18} that at any temperature greater than $T_{\gamma a}$ and $T_{\gamma b}$ for cases 'a' and 'b' respectively (Fig. 6.19), reaustenitisation should cease as soon as the residual austenite carbon concentration reaches the $A_{c3}$ curve, i.e. when

$$x_\gamma = x_{A_{c3}}(T_{\gamma a}) \quad (6.6)$$

Also, a temperature $T_{\gamma f}$ (Fig. 6.19) above which the alloy can transform completely into austenite satisfies the condition

$$x_{A_{c3}}(T_{\gamma f}) = \bar{x} \quad (6.7)$$

It can be established from the Fig. 6.19 as the average carbon content of the alloy $\bar{x}$ predicted that the specimen should transform completely to austenite at 760 °C and the metallographic confirmation of this can be seen in Fig. 6.20 and 6.21.

### 6.4 Conclusions

Reaustenitisation from a mixture of bainite and austenite has been studied isothermally under conditions where the nucleation of austenite is not necessary. The dilatometric results can be explained well by a theory for reaustenitisation proposed by Yang and Bhadeshia\cite{18}. Specimens partially transformed to bainitic ferrite and carbon enriched residual austenite, comparison of the volume fractions of austenite obtained in homogeneous and heterogeneous samples bearing in mind that the two kinds of samples do not have equivalent starting microstructures and hence carbon content of austenite is different in the two cases. As previously (Table 3.4) higher volume fractions of bainite were obtained in the homogeneous alloy its reaustenitisation start temperature will be lower than the heterogeneous alloy. The temperature at which the completion of reaustenitisation occurs, being dependent on average carbon content of the alloy $\bar{x}$, should be the same for homogeneous and heterogeneous alloys.
Fig. 6.1: Schematic illustration of heat treatments used in the experiments.

(a) Time versus temperature curve.

(b) Time versus relative length change curve.
Fig. 6.2: Typical dilatometric curves showing firstly the partial decomposition of austenite to the maximum amount of bainitic ferrite that can form at the transformation temperature concerned. In the second stage, the mixture of bainitic ferrite and carbon enriched austenite is rapidly heated to a temperature where it is thermodynamically possible for the austenite to grow.

(a) Sample transformed initially to bainite at $T_B=400 \, ^\circ C$ and then it is isothermally reaustenitised at $T_\gamma=730 \, ^\circ C$.

(b) Sample transformed initially to bainite at $T_B=320 \, ^\circ C$ and then it is isothermally reaustenitised at $T_B=740 \, ^\circ C$.  

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Fig. 6.3: Calculated\textsuperscript{[16,20]} phase boundaries for 300M steel along with the experimental data for samples transformed isothermally to upper bainite until the reaction ceased.

(a) Calculated $T_0$, $T_0'$ and $A_{c3}'$ phase boundaries assuming a chemically homogeneous alloy. All the points on the diagram are experimental data.

(b) Calculated $T_0$ and $A_{c3}'$ phase boundaries for the heterogeneous alloy, the shaded regions covering the range of chemical compositions detected experimentally.
Fig. 6.4: The effect of heating rate in suppressing any decomposition of residual austenite, prior to the sample reaching \( T_\gamma \).

(a) Heating rate = 11 °C s\(^{-1}\).

(b) Heating rate = 100 °C s\(^{-1}\).
Fig. 6.5: Graphs showing the relative length change obtained as a function of time during isothermal reaustenitisation at a variety of temperatures. The samples were all initially transformed at 320 °C to obtain a mixed starting microstructure of bainitic-ferrite and carbon-enriched residual austenite.
Fig. 6.6: Graphs showing the relative length change obtained as a function of time during isothermal reaustenitisation at a variety of temperatures. The samples were all initially transformed at 400 °C to obtain a mixed starting microstructure of bainitic-ferrite and carbon-enriched residual austenite.
Fig. 6.7: The relative length change versus temperature curves, of samples which were transformed initially to a mixture of bainitic ferrite and austenite at $T_B=320 \, ^\circ C$, prior to reaustenitisation at a variety of temperatures.

(a) Isothermal reaustenitisation at $720 \, ^\circ C$, from a starting microstructure of bainitic ferrite and austenite. The maximum relative length change can in this case be measured directly as the difference between points 'a' and 'b'.

(b) Isothermal reaustenitisation at $770 \, ^\circ C$ from a starting microstructure of bainitic ferrite and austenite. Because of the high value of $T_\gamma$, some austenite is seen to form during heating before the sample reached its designated isothermal reaustenitisation temperature. The distance 'a $-$ a' is therefore added to 'a $-$ b' (the relative length contraction at $T_\gamma$) to correct for this prior reaction.
Fig. 6.8: Magnitudes of the maximum relative length change obtained during isothermal reaustenitisation of heterogeneous samples, as a function of the isothermal reaustenitisation temperature $T_\gamma$. The absolute relative length changes given here are, in fact, negative as the growth of austenite at the expense of ferrite results in an increase in density. Data from two different starting microstructures, contain different amounts of residual austenite, are presented.
Fig. 6.9: Micrographs showing the extent of bainitic-ferrite formation and the amount of carbon enriched residual austenite obtained by reaction at $T_B$, before rapid heating to different reaustenitisation temperatures.

(a) Optical micrograph of a heterogeneous specimen isothermally transformed at $T_B=320$ °C.

(b) Optical micrograph of heterogeneous specimen isothermally transformed at $T_B=400$ °C, where the amount of bainitic ferrite that can form is much more limited.
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<th>Experimental Volume Fraction</th>
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Table 6.1: Dilatometrically determined maximum volume fractions of bainitic ferrite obtained by isothermal transformation at the temperatures indicated, for both the as-received and the homogenised samples of 300M steel.
Fig. 6.10: Comparison of homogeneous and heterogeneous samples after partial reaustenitisation at 740 °C. Both the samples were initially transformed at 320 °C to obtain a mixed starting microstructure of bainitic-ferrite and carbon-enriched residual austenite.

(a) Homogeneous alloy.

(b) Heterogeneous alloy.
Fig. 6.11: A partially reaustenitised heterogeneous sample showing differences in the extent of the reaction. The reaction has proceeded to a larger extent along the solute enriched bands, whose lower $A_{e3}$ temperature causes them to transform first.
Fig. 6.12: Relative length changes recorded during the quenching of heterogeneous samples after isothermal reaustenitisation at the temperature $T_\gamma$ indicated in each diagram. The specimens were transformed to bainitic ferrite and carbon enriched residual austenite formed at $T_B=320\,^\circ\text{C}$ prior to reaustenitisation.
Fig. 6.13: Relative length changes recorded during the quenching of heterogeneous samples after isothermal reaustenitisation at the temperature $T_\gamma$ indicated in each diagram. The specimens were transformed to bainitic ferrite and carbon enriched residual austenite formed at $T_B=400 \, ^\circ C$ prior to reaustenitisation.
Fig. 6.14: Dilatometrically measured martensitic-start temperatures as the heterogeneous samples reaustenitised at different temperatures were quenched to ambient temperature. The specimens were transformed to bainitic ferrite and carbon enriched austenite at 320 °C prior reaustenitisation.

Fig. 6.15: Calculated carbon concentrations of austenite formed after the heterogeneous specimens were reaustenitised at a variety of temperatures. The calculations are based on dilatometrically measured values of martensitic-start temperatures as shown in Fig. 6.14.
Fig. 6.16: Dilatometrically measured martensitic-start temperatures as the samples reaustenitised at different temperatures were quenched to ambient temperature. The specimens were transformed to bainitic ferrite and carbon enriched austenite at 400 °C prior to reaustenitisation.

Fig. 6.17: Calculated carbon concentrations of austenite formed after specimens were reaustenitised at different temperatures. The calculations are based on dilatometrically measured values of martensitic-start temperatures shown in Fig. 6.16.
Fig. 6.18: Calculated\textsuperscript{[21,22]} martensite start temperatures of austenite with different carbon content for 300M steel. A linear relation (eq. 6.1) was obtained by fitting a curve to this data with correlation coefficient of -0.99.
Fig. 6.19: Schematic phase diagram of a heterogeneous material with average carbon content $\bar{X}$. $A_{e3}$ and $T_0$ curves have been represented by a set of lines covering a composition range.
Reaustenitisation proceeds from solute enriched region to solute depleted region.

At lower T

At higher T

DISTANCE

Fig. 6.20: Schematic diagram showing the variation of $A_{e3}$ temperature in a heterogeneous alloy and its effect on growth of austenite.
Fig. 6.21: Calculated $A_{e3}$ and $T_0$ phase boundaries for heterogeneous 300M steel, covering the range of chemical compositions detected experimentally. $T_0$ curve is calculated as in Refs. [16,20] and the $A_{e3}$ curve is calculated as in Ref. 24.
Fig. 6.22: Metallographic confirmation of the curves shown in Fig. 6.5. The samples were initially transformed to bainitic ferrite and carbon enriched residual austenite at 320 °C.

(a) Optical micrograph of the heterogeneous specimen isothermally reaustenitised at 720 °C.

(b) Optical micrograph of the heterogeneous specimen isothermally reaustenitised at 730 °C.
Fig. 6.22: (continued.....)

(c) Optical micrograph of the heterogeneous specimen isothermally reaustenitised at 740 °C.

(d) Optical micrograph of the heterogeneous specimen isothermally reaustenitised at 750 °C.
Fig. 6.22: (continued.....)

(e) Optical micrograph of the heterogeneous specimen isothermally reaustenitised at 760 °C.

(f) Optical micrograph of the heterogeneous specimen isothermally reaustenitised at 770 °C.
Fig. 6.23: Metallographic confirmation of the curves shown in Fig. 6.6. The samples were initially transformed to bainitic ferrite and carbon enriched residual austenite at 400 °C.

(a) Optical micrograph of the heterogeneous specimen isothermally reaustenitised at 700 °C.

(b) Optical micrograph of the heterogeneous specimen isothermally reaustenitised at 715 °C.
Fig. 6.23: (continued.....)

(c) Optical micrograph of the heterogeneous specimen isothermally reaustenitised at 730 °C.

(d) Optical micrograph of the heterogeneous specimen isothermally reaustenitised at 760 °C.
REFERENCES


Chapter 7

ALLOTRIOMORPHIC FERRITE FORMATION
IN A HETEROGENEOUS STEEL

7.1 Introduction

Allotriomorphic ferrite is the first phase to form by the reconstructive transformation of austenite in low alloy steels, when the austenite is cooled below the $A_{e3}$ temperature\textsuperscript{[1,2]}. It nucleates at the austenite grain boundaries and in low alloy steels can eventually form continuous polycrystalline layers decorating the grain surfaces. Subsequent growth then essentially involves the one dimensional thickening of these layers into the remaining austenite. During the growth of the ferrite, the carbon partitions into the residual austenite ahead of austenite/ferrite interface so that the driving force for $\gamma \rightarrow \alpha$ transformation is decreased. Eventually, when the equilibrium volume fraction is achieved, the driving force is reduced to zero and interface motion ceases. The fundamental aspects of allotriomorphic ferrite have recently been reviewed\textsuperscript{[3]}.

Variations in alloy content lead to differences in the driving force for transformation, which may have a strong effect on nucleation and the subsequent growth of allotriomorphic ferrite. This has important consequences in the prediction of microstructure. The work presented here is an investigation of the paraequilibrium formation of ferrite in a heterogeneous alloy of average composition Fe-0.2C-1.37Mn-0.35Si wt. %.

7.2 Theoretical Analysis

The lever rule suggests that the maximum volume fraction of ferrite that can form at any given temperature should vary linearly with the average carbon content of the steel concerned. However, it has been reported\textsuperscript{[4]} that this relation does not hold for chemically heterogeneous steels. Bhadeshia\textsuperscript{[5]} presented a model for ferrite formation in heterogeneous dual-phase steels which explained these data, and suggested that the effect of segregation should vary with undercooling. This model was discussed in terms of a ternary alloy, \textit{e.g.}, Fe-Mn-C, of average Mn concentration $\overline{Mn}$, but with local variations ranging between the limits $Mn_{\text{min}}$ and $Mn_{\text{max}}$. In his simplified model, the transformation was considered to take place by the motion of a planar $\gamma/\alpha$ interface.
is normal to the isoconcentration planes, as illustrated in Fig. 7.1. The position of this interface, with respect to \( Z \), at any instant thus defines the volume fraction \( V \) of ferrite, i.e., \( V = Z \), reaching its maximum value of unity when the interface reaches the position where \( Mn = Mn_{\text{max}} \).

At relatively high temperatures (above the \( A_{\alpha 3} \) of the homogeneous alloy), the interface is expected to stop at a point where \( Mn < \overline{Mn} \) as shown in Fig. 7.2a. There will then be some transformation in the heterogeneous sample but none in the homogeneous alloy. This situation will continue until the interface reaches a stage where \( Mn = \overline{Mn} \) (Fig. 7.2b) i.e., the temperature falls to below the \( A_{\alpha 3} \) temperature of the homogeneous alloy. The model then suggests that transformation will occur to an identical extent, in both the heterogeneous and homogeneous samples. Beyond this point (Figs. 7.2c and 7.2d) it is expected that there should be more transformation in the homogeneous sample relative to that in the segregated sample.

7.2.1 Computer Simulation of the Published Model[5]

As will be seen later, circumstances may arise where the transformation front does not necessarily advance in a direction normal to the isoconcentration surfaces. The problem is here investigated by developing a computer model, whose performance is first checked against Bhadeshia's analytical approach.

The computer program was designed to simulate the development of ferrite formation in chemically heterogeneous steels. In this model, consistent with the previous work[5], the substitutional solute was assumed to vary linearly with distance as illustrated in Fig. 7.3 although the program is able to adopt any arbitrary composition profiles. The heterogeneous steel was represented as a composite of \( N \) slices of equal thickness (Fig. 7.4). Each slice, identified by a subscript \( i \), was assigned a different chemical composition within the range of experimental measurements of the minimum and maximum alloy content (Fig. 7.5). Microanalysis experiments were carried out using energy dispersive X-ray analysis (interaction volume approximately 4.5 \( \mu m^3 \)) on a scanning electron microscope. The composition within each slice was set to be uniform. The mean composition of all the slices was set to be identical to the mean composition of the as-received steel.

The calculation begins with the complete transformation of the first slice in the solute-depleted region (i.e., \( i = 1 \)), given that its \( A_{\alpha 3} \) temperature \( (T_{A_{\alpha 3}}^i) \) is higher than
the isothermal transformation temperature $T$ and at the same time $x_\gamma = \bar{x}$ is also less than its $x_{A_{\alpha}}$, which is the maximum carbon that can be tolerated by the austenite transforming under paraequilibrium conditions. $x_\gamma$ and $\bar{x}$ are the carbon concentrations of the residual austenite and of the average carbon content of the alloy respectively. This transformation changes the carbon concentration of the residual austenite $x_\gamma$ according to the following simple mass balance equation.

$$x_\gamma = \bar{x} + \frac{i}{N}(\bar{x} - x_{\alpha}) \left(1 - \frac{i}{N}\right)$$

(7.1)

Where, $\frac{i}{N} = V$ is the total volume fraction of ferrite when $i$ number of slices are able to transform. $x_{\alpha}$ is the amount of carbon which is left in the ferrite assumed to be 0.03 wt. %.

The growth of allotriomorphic ferrite in dilute steels generally occurs without the bulk partitioning of substitutional alloying elements[6], especially when the growth rates involved are large[7]. Only carbon then partitions during growth. In such circumstances, ferrite growth can occur at a rate controlled by the diffusion of carbon in the austenite ahead of the interface. In these calculations it was, therefore, assumed that $\alpha$ growth occurs by a carbon diffusion paraequilibrium[8–12] mechanism so that substitutional alloying elements do not partition at all between the phases; carbon then partitions to an extent which allows its chemical potential to be identical in all phases.

Hence, transformation is only allowed to continue in the next slice $i$ if for that slice $x_\gamma < x_{A_{\alpha}}$. The calculation is stopped at a slice $i$ when $x_\gamma = x_{A_{\alpha}}$ as illustrated in Fig. 7.4.

**7.2.2 Results and Discussion**

The results obtained from the simulation of the Bhadeshia model[5] are shown in Fig. 7.6. At low undercoolings a greater volume fraction of ferrite was obtained in the heterogeneous alloy compared with the homogeneous alloy. Both volume fractions increased on decreasing temperature but their difference decreased until a crossover point after which the situation is reversed. It can be seen from Fig. 7.7 that the number of transforming slices decreased with an increase in the isothermal transformation temperature. During the course of transformation at any specified temperature, the amount of carbon that can be tolerated by the austenite decreases while at the same
time, the carbon content of the residual austenite goes on increasing. The point where these two curves meet gives the limiting volume fraction of ferrite. These results are in good agreement with the predictions forwarded by Bhadeshia[5].

Although the model is a good representation of transformation in a heterogeneous sample during continuous cooling, it might not be applicable under isothermal transformation conditions. If the driving force for transformation is large, the initial nucleation and growth of ferrite may not be restricted to the solute-depleted region. The nucleation and growth of ferrite can start at more than one place in case of isothermal transformation at large undercoolings. In these circumstances it is no longer reasonable to expect the transformation front to proceed from the solute-depleted to the solute-enriched regions, but reaction may occur everywhere.

To study this, the computer model was arranged to permit the motion of the $\gamma/\alpha$ interface to occur parallel to the isoconcentration planes as shown in Fig. 7.8. The calculation was carried out in incremental stages (Fig. 7.9), with each stage identified by the subscript $j$. It should be noted that each incremental step of transformation now happens in a direction normal to the isoconcentration planes, so that several slices could be reacting at any instant. The computation begins with all the slices being fully austenitic. For the first step ($j = 1$) $A_{e3}$ temperatures are calculated for all the slices. If for any slice, $T_{Ae3}^i < T$ then that slice remains untransformed throughout the experiment. For slices which are below their $T_{Ae3}^i$ temperatures, a small amount of ferrite is permitted to form, giving a volume fraction increment of $\Delta V$. This increment of transformation changes the carbon concentration in the unreacted regions of the slices according to a simple mass balance equation

$$x_{i\gamma} = x + \frac{V_{ij}(x - x_\alpha)}{(1 - V_{ij})}$$  \hspace{1cm} (7.2)

where $V_{ij}$ and $x_{i\gamma}^j$ are, respectively, the total volume fraction of ferrite, and the total carbon concentration of the residual austenite in slice $i$ at stage $j$ of the calculation.

Hence, for $j > 1$, an increment of transformation is only allowed in any given slice if for that slice $x_{i\gamma}^j < x_{Ae3}^i$. $x_{Ae3}$ is the carbon that can be tolerated by the austenite transforming under paraequilibrium conditions. The mean volume fraction of transformation in the alloy as a whole at stage $j$ is given by:

$$\bar{V}_j = \sum_i V_{ij}/N.$$  \hspace{1cm} (7.3)

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The calculation is stopped when all slices cease to transform; $x^i_j = x^i_{Ae3}$ for all $i$.

We consider first the case where the slices transform independently of each other, i.e., without any homogenisation of carbon between the slices. The results thus obtained are shown in Fig. 7.10 which illustrate that as long as the alloy is transformed below the $Ae3$ temperature of the homogeneous alloy, there is no difference of volume fractions between the homogeneous and heterogeneous samples. This might be due to the fact that the composition variations detected here are not large enough to produce a remarkable difference in volume fractions of allotriomorphic ferrite in homogeneous and heterogeneous samples. Moreover, due to the small slope of the $Ae3$ curve, the effect of chemical heterogeneity in shifting the $Ae3$ temperature is less as compared to that on $B_s$ while considering the slope of $T_0$ curve.

On the other hand, if transformation was induced at temperatures above the $Ae3$ temperature of the homogeneous alloy, ferrite formation obviously does not occur in the homogeneous sample, but some slices are able to transform in the heterogeneous sample.

At higher undercoolings, the nucleation and growth of ferrite is restricted to the solute depleted regions of the heterogeneous alloy, with relatively rapid reaction in those regions compared with the homogeneous alloy. The reaction in the segregated alloy will always be faster than the homogenised alloy. Limited transformation in the solute-enriched regions appears to be compensated by the ease of transformation in the solute-depleted regions.

At still higher undercoolings, nucleation and growth becomes possible everywhere in both the homogeneous and heterogeneous samples, i.e., at these temperatures all the slices are able to transform to ferrite to a greater or lesser extent. Growth is then expected to be limited by the carbon enrichment of the residual austenite. For the case considered here, where it is assumed that excess carbon cannot redistribute between slices, the untransformed regions of the heterogeneous sample which are rich in substitutional alloy content, are unable to act as sinks for the excess carbon, so as to allow further transformation in the substitutional solute-depleted regions. When compared with bainite, the allotriomorphic ferrite carbon diffusion field in the austenite will be relatively large partly due to the higher transformation temperatures involved and partly because of the large size and less convoluted morphology of the growing
phase. The significance of this effect can be examined theoretically using the computer model with the additional condition that after every increment $\Delta V$ of transformation, the carbon is allowed to redistribute and homogenise between the slices. This should permit the solute-enriched regions to act as sinks for any excess carbon, thereby facilitating further transformation in the solute-depleted regions. The results (Fig. 7.10) show that if carbon is permitted to homogenise in the residual austenite after every increment of transformation, the volume fraction of transformation in the heterogeneous samples should always exceed that in the homogenised samples. The difference between the two cases decreases with an increase in undercooling.

7.3 Dilatometry

Dilatometric experiments were carried out to compare the experimental results with the predictions made by the models described above. The specimens were austenitised at 1000 °C for 10 minutes before helium gas quenching to a variety of isothermal transformation temperatures within the range where the reconstructive growth of ferrite alone is expected. The length change during the isothermal reaction was measured and the corresponding relative length change versus time data plotted as in Fig. 7.11. The optical micrographs in Fig. 7.12 give a comparison of the extent of transformation in the homogeneous and heterogeneous samples. The relative length change corresponding to a volume fraction of ferrite transformed $V_b$ is given by:

$$\frac{\Delta l}{l} = \frac{2V_b a_\alpha^3 + (1 - V_b) a_\gamma^3 - \bar{a}_\gamma^3}{3\bar{a}_\gamma^3}$$  \hspace{1cm} (7.4)

where $a_\alpha$ is the lattice parameter of ferrite at the transformation temperature, given by:

$$a_\alpha = a_\alpha^o [1 + e_\alpha (T - 25)]$$  \hspace{1cm} (7.5)

and $\bar{a}_\gamma$, which is the lattice parameter of austenite of the alloy composition at the transformation temperature, is given by:

$$\bar{a}_\gamma = (a_\gamma^o + \Sigma c_i x_i) [1 + e_\gamma (T - 25)].$$  \hspace{1cm} (7.6)

In these equations, $e_\alpha$ and $e_\gamma$ represent the linear thermal expansivities of ferrite and austenite respectively, $a_\alpha$ is the lattice parameter of austenite in pure iron at 25 °C, $x_i$
is the concentration of alloying element \( i \) and \( c_i x_i \) represents the change in \( a_o \) due to the addition of the alloying elements to pure iron. \( T \) is the temperature in °C.

The ferrite linear expansion coefficient was determined by first tempering a specimen at 600 °C for 10 minutes to decompose any retained austenite and then recording the length change during very slow cooling. The measurements do not therefore account for the presence of any carbide, whose volume fraction is in any case expected to be negligibly small for the present purposes.

The graph of relative length versus temperature is plotted in Fig. 7.13, from which the linear expansion coefficient of ferrite was found to be \( e_{\alpha} = 9.847 \times 10^{-6} \text{ K}^{-1} \). The expansion coefficient of austenite was measured while specimen was in the single-phase field, as shown in Fig. 7.14 (\( e_{\gamma} = 2.122 \times 10^{-5} \text{K}^{-1} \)). The ferrite lattice parameter (\( a_\alpha^o \)) at ambient temperature was measured using a Debye-Scherrer technique. The test specimen was annealed at 600 °C for half an hour, and then machined to the form of 0.5mm x 0.5mm x 15mm wire. It was then immersed in an aqueous solution made up of 5% HF and 45% \( \text{H}_2\text{O}_2 \) (by volume) for two minutes to remove the deformation layer before testing. The specimens were irradiated with Mo \( \text{K}_\alpha \) radiations using a standard Debye-Scherrer camera. A value of lattice parameter was calculated for each reflection from the resulting photograph and plotted against the Nelson-Riley function\[^{[13]}\] of Bragg angle \( \theta \). Linear regression technique was used to extrapolate a best-fit line back to \( \theta = 90^\circ \), to find the intercept and the standard error in the intercept (Fig. 7.15). The resulting value of lattice parameter was found to be as \( 2.8675 \pm 0.0015 \text{ Å} \) which is in good agreement with the value calculated to be \( 2.8667 \text{ Å} \) using data from Leslie\[^{[14]}\]. With these measured values and making the appropriate substitutions in equation 7.4, the volume fractions of ferrite transformed could be deduced using a computer program.

7.3.1 Results and Discussion

The carbon content of residual austenite when isothermal transformation ceases is very useful in understanding the transformation mechanism. The maximum relative length change was converted into the volume fraction of ferrite transformed, from which the carbon content of the residual austenite can be calculated using equation 7.1. It should be noted that no carbide precipitation was observed even at the lowest isothermal transformation temperature considered here which is 700 °C. That is evident from the transmission electron micrograph shown in Fig. 7.16 of the sample isothermally
transformed at 700 °C. Isothermal transformation experiments were carried out over the temperature range 700-760 °C. The data thus obtained are plotted on a phase diagram as shown in Fig. 7.17. It is clear that for the short time heat treatments studied here, the reaction becomes imperceptibly slow before the austenite reaches its equilibrium composition. Hence, the assumption involved in the slice model, that the growth of \( \alpha \) occurs under paraequilibrium conditions, seems reasonable.

The experimental data provided in Fig. 7.17 are not sufficiently extensive to confirm how the volume fraction of ferrite in a heterogeneous alloy should differ from a homogeneous alloy but the comparison available at two temperatures (i.e., 700 and 740 °C) shows that more transformation is obtained in heterogeneous sample. This is supported by the results obtained from the slice model, provided the carbon is allowed to homogenise among the slices. The data obtained at 730 °C are not consistent with the rest of the experiments as it shows lesser transformation than that observed at 740 °C. No obvious reasons could be found for this discrepancy, which is tentatively assigned to experimental error.

7.4 Conclusions

Allotriomorphic ferrite formation in a heterogeneous alloy has been modelled for situations equivalent to "continuous cooling" and isothermal transformation. In the first case, the \( \gamma/\alpha \) transformation front was considered to move normal to the isoconcentration planes, i.e., from solute-depleted region to solute-enriched region. The results support the published predictions\(^5\) that below the volume fraction of 0.5, there will be more transformation in a heterogeneous alloy than the homogeneous alloy while above the volume fraction of 0.5 the situation is reversed.

For isothermal transformation, the motion of \( \gamma/\alpha \) transformation front was considered to be parallel to the isoconcentration planes. At any undercooling below \( A_{\gamma/\alpha} \) temperature of the homogeneous alloy, limited nucleation (in the areas whose alloy content is either equal or below the average alloy content) in the heterogeneous alloy can be compensated by the faster growth in the solute depleted regions. Moreover, due to higher transformation temperatures involved, carbon can distribute evenly throughout the residual austenite to facilitate still more transformation. It is found that the extent
of transformation is always larger for the heterogeneous samples when compared with the homogenised samples.

The model is based on the hypothesis that the growth of $\alpha$ occurs under paraequilibrium conditions. The experimental results presented here support this hypothesis, and provide a new way of deducing the paraequilibrium mode of transformation.
Fig. 7.1: In the model for allotriomorphic ferrite in heterogeneous steels\textsuperscript{[5]}, the growth direction of the ferrite is considered to be normal to the isoconcentration planes.
Fig. 7.2: Schematic representation of the position of the $\gamma/\alpha$ interface in a heterogeneous alloy. The coordinate ‘$z$’ is defined to be normal to the planes of constant composition and is normalised with respect to the specimen length in the $Z$-direction. Four different positions of the interface are shown:
(a) when $Mn < \overline{Mn}$,
(b) when $Mn = \overline{Mn}$,
(c) when $Mn > \overline{Mn}$,
(d) when $Mn = M_{n\text{max}}$. 
Fig. 7.3: Graph showing the linear variation of Mn and Si concentrations as a function of distance (slice number) as utilised in the slice model presented in the text.
Choose $T, N$

Set $V_i = 0$
For all $i$
$x_{\gamma} = \bar{x}$

Calculate $x_{A_{\gamma3}}^i$ & $T_{A_{\gamma3}}^i$

If $T_{A_{\gamma3}}^i < T$

If $x_{\gamma} < x_{A_{\gamma3}}^i$

$V = i/N$
Calculate New $x_{\gamma}$

$i = i + 1$ 

If $i = N$?

STOP

Fig. 7.4: Flow chart illustrating the calculation procedure used to simulate the development of transformation in a heterogeneous steel while the $\gamma/\alpha$ interface moves normal to the isoconcentration planes in accordance with the Bhadeshia model[5].
Fig. 7.5: Microanalysis data from heterogeneous sample of Fe-0.17C-0.35Si-1.38Mn wt.% steel which was austenitised at 1000 °C and then transformed isothermally at 700 °C for 60 minutes. The error bars indicate the typical 95% confidence statistical error and the average composition is in each case indicated by the dashed horizontal line.

Fig. 7.6: Calculated ferrite volume fraction as a function of isothermal transformation temperature in a heterogeneous alloy as the growth direction of the \( \gamma/\alpha \) interface was considered to be normal to the isoconcentration planes.
Fig. 7.7: Illustration of how the paraequilibrium carbon concentration and the actual carbon concentration of the residual austenite converge as the transformation front advances into solute-enriched regions.
Fig. 7.7: (continued .... )
Fig. 7.8: In another model for allotriomorphic ferrite in heterogeneous steels, the growth direction of the ferrite can be considered to be parallel to the isoconcentration planes.
Choose T, N
Set \( V_i = 0 \)
For all i
Calculate \( z_{A+e}, T_{A+e}^i \)
For all i
\( x_i^j = x_i^e \)
\( T_{A+e}^i < T_i \)
No
Yes
\( x_i^j < x_i^{A+e} \)
\( V_{ij} = V_{ij} + 0 \)
\( V_{ij} = V_{ij} + \Delta V \)
Yes
No
\( i = i + 1 \)
Is i = N ?
Yes
\( \bar{V}_j = \sum V_{ij} / N \)
No
STOP
Have all slices stopped transforming?
Yes
\( j = j + 1, i = 1 \)
No

Fig. 7.9: Flow chart illustrating the calculation procedure used to simulate the development of transformation in a heterogeneous steel. \( T_i \) represents the isothermal transformation temperature and the subscript \( i \) identifies the slice number and composition; the total number of slices is \( N \). The calculation is carried out in stages, with each stage identified by the subscript \( j \). For each value of \( j \) (i.e., at each stage of the calculation), the volume fraction \( V_{ij} \) of ferrite in each slice is incremented by a small fraction \( \Delta V \) if transformation is feasible in that slice. The total volume fraction of ferrite at stage \( j \) is thus given by \( \sum_i V_{ij} / N \).
Fig. 7.10: Comparison of maximum volume fraction transformed in homogeneous and heterogeneous samples as calculated by the slice model in which $\gamma/\alpha$ interface was assumed to move in a direction parallel to the isoconcentration planes. The line has a slope of unity, and serves to show that except above the $A_{\gamma 3}$ of the homogeneous sample (where the degree of transformation is larger in case of heterogeneous sample) there is no significant difference between the two, provided the slices are allowed to transform independent of each other. But if an opportunity is provided for carbon to distribute evenly throughout the residual austenite, the extent of transformation is always larger in the heterogeneous samples.
Fig. 7.11a: Dilatometric curves for Fe-0.17C-0.35Si-1.38Mn wt. % steel isothermally transformed at the temperatures indicated. The continuous curves are for the homogenised samples and the dashed curves for the heterogeneous samples.
Fig. 7.11b: Dilatometric curves for the homogenised Fe-0.17C-0.35Si-1.38Mn wt. % steel isothermally transformed at the temperatures indicated.
Fig. 7.11c: Dilatometric curves for the heterogeneous Fe-0.17C-0.35Si-1.38Mn wt.% steel isothermally transformed at the temperatures indicated.
Fig. 7.12: Metallographic confirmation of the curves shown in Fig. 7.9a.
(a) Optical micrograph of the homogeneous specimen isothermally transformed at 700 °C.
(b) Optical micrograph of the heterogeneous specimen isothermally transformed at 700 °C.
Fig. 7.12: (continued...)

(c) Optical micrograph of the homogeneous specimen isothermally transformed at 740 °C.

(d) Optical micrograph of the heterogeneous specimen isothermally transformed at 740 °C.
Fig. 7.13: Graph of relative length change versus temperature, from which the linear expansion coefficient of ferrite is obtained.

Fig. 7.14: Graph of relative length change versus temperature, from which the linear expansion coefficient of austenite is obtained.
Fig. 7.15: Extrapolation of measured lattice parameter against Nelson-Riley function (i.e., $\cos^2 \theta + \frac{\cos^2 \theta}{\sin \theta}$). $\theta$ is the diffraction angle.

Fig. 7.16: Bright field transmission electron micrograph from a heterogeneous sample of Fe-0.17C-0.35Si-1.38Mn wt. % steel, transformed isothermally to allotriomorphic ferrite at 700 °C for 60 minutes before quenching to ambient temperature. Shows allotriomorphic ferrite and residual austenite.
Fig. 7.17: Calculated $T'_0$, $A'_{e3}$ and $A_{e3}$ phase boundaries for Fe-0.17C-0.35Si-1.38Mn wt.% steel. The experimental data are for samples transformed isothermally to allotriomorphic ferrite.
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Chapter 8

COMPLETE CALCULATION OF MICROSTRUCTURAL EVOLUTION IN HETEROGENEOUS AUTOMOBILE STEELS

8.1 Introduction

In the previous chapters, various aspects of the transformation of austenite to allotriomorphic ferrite, bainite and martensite in a heterogeneous alloy were discussed. Moreover, some models were presented to help predict the volume fractions and other characteristics of these transformation products both for homogeneous and for chemically segregated steels. The purpose of the work presented in this chapter was to use to apply the models to some new steels which are being developed at Inland Steel (USA) for automobile crash reinforcement bars. The steels are at an early stage of development and could benefit from fundamental alloy design. Cars manufactured in the old days had door panels which were very thick (~20 cm), and consequently could be reinforced against sidewise impact using relatively low strength steel in the form of zig-zag concertina type rectangular rods incorporated within the doors. Modern cars however have thinner panels which are reinforced by high-strength steel bar (the present steels are candidate alloys) running across the panels, in a way which transmits any impact into the structural frame, thereby ensuring the passenger safety. The steels 'US83' and 'US24' are of average compositions Fe-0.20C-0.63Si-2.80Mn-0.04Ni-0.01Mo-1.10Cr wt.% and Fe-0.18C-0.75Si-1.98Mn-0.02Ni-0.01Mo-1.33Cr wt.% respectively. The interesting feature of the alloys is their relatively high silicon concentration, and their bainite microstructure, of the type discussed earlier.

8.2 Dilatometry

Dilatometry was used to study the development of transformation. The specimens were austenitised at 1000 °C for 10 minutes before helium gas quenching to a variety of isothermal transformation temperatures within the bainite transformation range (Fig. 8.1). The length change during the isothermal reaction was measured and the corresponding relative length change versus time data plotted as in Figs. 8.2 and 8.3. The interesting feature of these sigmoidal curves is once again, that the maximum
extent of transformation (i.e., the maximum value of relative length change) at any temperature decreases with increasing isothermal transformation temperature and this is expected from the slope of the \( T_0 \) curve as discussed earlier. These results are supported by optical microscopy as seen in Figs. 8.4 and 8.5 which also gives a visual comparison of the extent of reaction in the homogeneous and heterogeneous samples. Banding is always apparent in the as-received alloy, although it seems to become less obvious at high degrees of transformation (i.e., at low transformation temperatures).

Figure 8.6 shows a typical dilatometric curve of the relative length change as a function of temperature for the two steels during cooling from the austenitising temperature to the lowest isothermal transformation temperature used in the present experiments. The linearity of the plot proves the absence of any transformation during the quench to the isothermal transformation temperature, so that the equipment used is clearly capable of permitting isothermal transformation experiments.

To reveal further information from the dilatometric experiments, the data were analysed as in previous chapters. The relative length change corresponding to a volume fraction of bainitic ferrite \( V_b \) that grows from austenite, is given by:

\[
\frac{\Delta l}{l} = \frac{2V_b a_\alpha^3 + (1 - V_b)a_\gamma^3 - \bar{a}_\gamma^3}{3a_\gamma^3}
\]  

(8.1)

where \( a_\alpha \) is the lattice parameter of ferrite at the transformation temperature, given by:

\[
a_\alpha = a_o^\alpha [1 + e_\alpha (T - 25)]
\]  

(8.2)

and \( \bar{a}_\gamma \), which is the lattice parameter of austenite of the alloy composition at the transformation temperature, is give by:

\[
\bar{a}_\gamma = (a_o^\gamma + \Sigma c_i x_i)[1 + e_\gamma (T - 25)].
\]  

(8.3)

In these equations, \( e_\alpha \) and \( e_\gamma \) represent the linear thermal expansivities of ferrite and austenite respectively, \( a_o \) is the lattice parameter of austenite in pure iron at 25 °C, \( x_i \) is the concentration of alloying element \( i \) and \( c_i x_i \) represents the change in \( a_o \) due to the addition of the alloying element to pure iron. \( T \) is the temperature in °C. The ferrite linear expansion coefficient was determined by first tempering a specimen at 600 °C for 10 minutes to decompose any retained austenite and then recording the length
change during very slow cooling. The measurements do not therefore account for the presence of any carbide whose volume fraction is in any case expected to be negligibly small for the present purposes. The graphs of relative length versus temperature are plotted in Fig. 8.7, from which the linear expansion coefficients of ferrite were obtained for the two steels ($\epsilon_\alpha = 1.022 \times 10^{-5}K^{-1}$ and $\epsilon_\alpha = 1.430 \times 10^{-5}K^{-1}$ for 'US83' and 'US24' steels respectively). The expansion coefficients of austenite were measured while specimens were in the single-phase field, as shown in Fig. 8.8 ($\epsilon_\gamma = 2.030 \times 10^{-5}K^{-1}$ and $\epsilon_\gamma = 2.230 \times 10^{-5}K^{-1}$ for 'US83' and 'US24' steels respectively).

The ferrite lattice parameter ($a_\alpha^0$) at ambient temperature was measured using a Debye-Scherrer technique. The test specimen was annealed at 600 °C for half an hour, and then machined in the form of 0.5mm × 0.5mm × 15mm wire. Finally the specimen was immersed in an aqueous solution made up of 5% HF and 45% H$_2$O$_2$ (by volume) for two minutes to remove the deformation layer before testing. The specimens were irradiated with Mo K$_\alpha$ radiations using a standard Debye-Scherrer camera. A value of lattice parameter was calculated for each reflection from the resulting photograph and plotted against the Nelson-Riley function$^1$ of Bragg angle $\theta$. The linear regression technique was used to extrapolate a best-fit line back to $\theta = 90^\circ$, to find the intercept and the standard error in the intercept (Fig. 8.9). The resulting values of lattice parameter came out as 2.8692 ± 0.0012 Å for 'US83' and 2.8670 ± 0.002 Å for 'US24' which are in agreement with the respective values calculated to be 2.8679 Å and 2.8675 Å using data from Leslie$^2$ but the steel has Mo, which is not included in the data from Leslie.

Using these measured values and making the appropriate substitutions in equation 8.1, the volume fractions of bainitic ferrite transformed were obtained using a computer program and the results thus obtained are shown in Figs. 8.10 and 8.11.

The range of concentration variation was found (Fig. 8.12 and 8.13) to be approximately 0.53-0.73Si,2.48-3.12Mn,1.03-1.17Cr wt. % for 'US83' steel and 0.60-0.90Si,1.65-2.31Mn,1.15-1.51Cr wt. % for 'US24' steel. Ni, Mo and V concentrations were too low to detect the corresponding small variations using microanalysis.
8.3 Transformation to Bainitic Ferrite

More transformation to bainite was observed in the homogenized samples as compared with the heterogeneous sample, at high undercoolings below the Bs temperature of the homogeneous sample (i.e., 465 °C) for both ‘US83’ and ‘US24’ steels. At low undercoolings, the extent of isothermal transformation is found to be larger in the heterogeneous samples. Typical microstructures, as characterised using transmission electron microscopy are illustrated in figures 8.14 and 8.15. Carbide-free upper bainite was obtained even at the lowest temperatures shown in these figures. The carbon content of residual austenite was calculated using following mass balance equation\(^3\).

\[
x_\gamma = \bar{x} + \frac{V_b(\bar{x} - x_\alpha)}{1 - V_b} \tag{8.4}
\]

where, \(V_b\) is the volume fraction of bainitic ferrite. \(x_\alpha\) is the amount of carbon which is left in the ferrite assumed to be 0.03 wt.%. \(\bar{x}\) is the actual carbon content of the alloy.

In this way, the carbon concentration in the austenite at the point where isothermal transformation ceases can be calculated, and a comparison of such data for upper bainite, with the \(T_0\), \(T'_0\) and \(A'_{e3}\) curves, calculated\(^3,4\) from the chemical composition of the homogeneous alloy, is presented in Figs. 8.16 and 8.17. The experimental results are more consistent with the \(T'_0\) curve relative to \(T_0\) curve. It is evident from these figures that the experimental data support the conclusion that the growth of bainite is diffusionless, with the carbon being partitioned subsequently into the residual austenite. The results show that both of these steels accurately exhibit the incomplete reaction phenomenon, which can be used to estimate theoretically the degree of transformation expected as a function of isothermal transformation temperature or in terms of the alloy chemistry.

8.3.1 Theoretical Analysis

The transformation behaviour of these steels was also studied theoretically using the slice model fully described in chapter 4 and compared with the experimental data in figures 8.18 and 8.19. In these calculations, The heterogeneous steel was represented as a composite of many slices of equal thickness but of different chemical composition consistent with the experimentally measured composition range. The \(\gamma/\alpha\) interface is
considered to move parallel to the isoconcentration planes as the microstructure shows banding.

In one case, the slices transform independently of each other, which is the more likely circumstance because of the sheaf morphology of bainite, where carbon trapped in the residual austenite remains isolated from one another.

The reasonable agreement is found in predicting the different behaviours of the as-received and homogenised samples. For most of the data, both theory and experiment show a higher degree of transformation in the homogenised samples, and both show a reversal of this trend as the transformation temperature approaches the $B_s$ temperature of the homogenised alloy. However, the difference in the calculated volume fraction of bainite in the homogeneous and heterogeneous “US24” steel samples was found to be negligible above the $B_s$ temperature of the homogeneous alloy. It should be noted that the “US24” steel not only has lower carbon content but Mn is also less than that in the “US83” steel which is affecting the transformation behaviour of the two steels. To make this point more clear, calculations were carried out for different compositions with varying average Mn content and also for different Mn variation ranges for the “US24” steel. In one case the average Mn content was varied keeping the Mn range constant as shown in Fig. 8.20a. The results were not very different as still the maximum Mn content considered (2.83 wt.%) was just the same as the average Mn concentration (2.80 wt.%) of the “US83” steel. So in another set of calculations the maximum Mn concentration of the heterogeneous “US24” steel was varied (up to 3.35 wt.%) while the minimum concentration was kept constant (i.e., 1.65 wt.%). Fig. 8.20b illustrates that as we increase the Mn content, the austenite can tolerate less and less carbon and the difference in the homogeneous and heterogeneous samples becomes more significant.

In another case of the slice model, carbon is allowed to distribute evenly throughout the residual austenite (i.e., among the slices) during the development of bainitic microstructure. The fact that the carbon does not homogenise during transformation is emphasized by the results shown in Figs. 8.18 and 8.19, where the calculated data (assuming that carbon homogenises between the slices) are seen to overestimate the volume fraction of bainite.
8.4 Martensitic Transformation in 'US83' Steel

The dilatometric specimens from the 'US83' steel of average composition Fe-0.20C-0.63Si-2.80Mn-0.04Ni-0.01Mo-1.10Cr wt. % were quenched to ambient temperature after an appropriate time of isothermal holding at different temperatures (T_b) in the bainite range. Dilatometric curves of relative length change versus temperature are shown in Fig. 8.21. These data were converted into the volume fraction of martensite (f) using the following relationship:

\[
\frac{3\Delta L a_\gamma^3}{V_\gamma L (2a_\alpha^2 c_\alpha - a_\gamma^3)}
\]

(8.5)

where \( a_\gamma \) is the lattice parameter of the the carbon-enriched residual austenite, \( a_\alpha \) and \( c_\alpha \) are the lattice parameters of tetragonal martensite, and \( V_\gamma \) is the volume fraction of austenite present in the sample prior to martensitic transformation. The absolute volume fraction of martensite \((V_\alpha')\) can be obtained by multiplying the fraction of austenite transformed to martensite \((f)\) with the actual volume fraction of austenite \((V_\gamma)\) initially present at \( T_B \), i.e.,

\[
V_\alpha' = fV_\gamma
\]

(8.6)

A computer program was written and used for these calculations which takes full account of the changes in lattice parameters as a function of alloy composition and temperature, as described elsewhere [5,6].

Another very useful information obtained from these dilatometric curves was the experimental measurement of the martensitic start temperature \((M_s)\) as the point where the curve deviates from straight line during cooling. A good agreement between the calculated [7,8] and measured \( M_s \) temperature of can be seen from the Fig. 8.22. All these data were further used in the theoretical study of the progress of the athermal martensitic transformation as described empirically by the following equation:

\[
1 - f = \exp\{-C_1(M_s - T_Q)\}
\]

(8.7)

where \( f \) is the volume fraction of martensite divided by the volume fraction of austenite prior to the formation of martensite, \( T_Q \) is a temperature to which the sample is cooled below \( M_s \); \( C_1 \) is a constant obtained originally [9] by fitting to experimental data. The comparison of the experimental and calculated volume fraction of martensite using the
above equation is shown in Fig. 8.23. As mentioned previously in chapter 5, the above empirical equation cannot predict the kinetics of martensite formation at all stages of the reaction. A new model, as described in chapter 5, was then used to study the development of martensitic transformation as a function of undercooling below the $M_S$ temperature. This model includes the effects of autocatalysis$^{[10-12]}$ and can be described by the following equation:

$$\frac{-\ln\{1 - f\}}{f} = 1 + \overline{V}C_6(M_S - T_q) \quad (8.8)$$

or

$$\frac{-\ln\{1 - f\}}{f} = 1 + C_7(M_S - T_q) \quad (8.9)$$

where $C_7 = \overline{V}C_6$. $\overline{V}$ is the average volume per newly formed martensite plate assumed to be constant for the course of these calculations.

Figure 8.24 shows that the new model can better predict the kinetics of the martensite reaction at all stages.

8.5 Conclusions

All the experimental and theoretical work presented in the previous chapters was tried and tested for two more heterogeneous steels. Figure 8.25 shows the cumulative results of the complete calculation of microstructure in the homogeneous and heterogeneous "US83" steel samples. As expected, more transformation to martensite was obtained with a decrease in the bainitic ferrite volume fraction. The results confirm that the models illustrated previously are valid for other steels also.
Fig. 8.1: Calculated\cite{4,13} time-temperature-transformation (TTT) diagrams.
(a) "US83" steel of average composition Fe-0.20C-0.63Si-2.80Mn-0.04Ni-0.01Mo-
1.10Cr wt. %.
(b) "US24" steel of average composition Fe-0.18C-0.75Si-1.98Mn-0.02Ni-0.01Mo-
1.33Cr wt. %.
Fig. 8.2: Dilatometric curves for samples of 'US3' steel isothermally transformed at the temperatures indicated. The continuous curves are for the homogenised samples and the dashed curves for the heterogeneous samples.
Fig. 8.3: Dilatometric curves for samples of 'US24' steel isothermally transformed at the temperatures indicated. The continuous curves are for the homogenised samples and the dashed curves for the heterogeneous samples.
Fig. 8.3: (continued....)
Fig. 8.4: Metallographic confirmation of the curves shown in figure 8.1:

(a) Optical micrograph of the homogeneous specimen, from 'US83' steel, isothermally transformed at 400 °C.

(b) Optical micrograph of the heterogeneous specimen, from 'US83' steel, isothermally transformed at 400 °C.

(c) Optical micrograph of the homogeneous specimen, from 'US83' steel, isothermally transformed at 420 °C.

(d) Optical micrograph of the heterogeneous specimen, from 'US83' steel, isothermally transformed at 420 °C.
(e) Optical micrograph of the homogeneous specimen, from 'US83' steel, isothermally transformed at 440 °C.

(f) Optical micrograph of the heterogeneous specimen, from 'US83' steel, isothermally transformed at 440 °C.
Fig. 8.4: (continued ..... )

(g) Optical micrograph of the homogeneous specimen, from 'US83' steel, isothermally transformed at 460 °C.

(h) Optical micrograph of the heterogeneous specimen, from 'US83' steel, isothermally transformed at 460 °C.
Fig. 8.5: Metallographic confirmation of the curves shown in figure 8.1:

(a) Optical micrograph of the homogeneous specimen, from ‘US24’ steel, isothermally transformed at 400 °C.

(b) Optical micrograph of the heterogeneous specimen, from ‘US24’ steel, isothermally transformed at 400 °C.

(c) Optical micrograph of the homogeneous specimen, from ‘US24’ steel, isothermally transformed at 420 °C.

(d) Optical micrograph of the heterogeneous specimen, from ‘US24’ steel, isothermally transformed at 420 °C.
Fig. 8.5: (continued .....)

(e) Optical micrograph of the homogeneous specimen, from 'US24' steel, isothermally transformed at 440 °C.

(f) Optical micrograph of the heterogeneous specimen, from 'US24' steel, isothermally transformed at 440 °C.

(g) Optical micrograph of the homogeneous specimen, from 'US24' steel, isothermally transformed at 460 °C.

(h) Optical micrograph of the heterogeneous specimen, from 'US24' steel, isothermally transformed at 460 °C.
Fig. 8.5: (continued ..... )

(i) Optical micrograph of the homogeneous specimen, from 'U524' steel, isothermally transformed at 480 °C.

(j) Optical micrograph of the heterogeneous specimen, from 'US24' steel, isothermally transformed at 480 °C.
Fig. 8.6: Dilatometric curves showing the linear variation of relative specimen length as a function of temperature during cooling from the austenitising temperature to the isothermal transformation temperature.

(a) Heterogeneous 'US83' steel.

(b) Heterogeneous 'US24' steel.
Fig. 8.7: Graph of relative length change versus temperature, from which the linear expansion coefficient of ferrite is obtained.
(a) 'US3' steel.
(b) 'US24' steel.
Fig. 8.8: Graph of relative length change versus temperature, from which the linear expansion coefficient of austenite is obtained.

(a) 'US83' steel.

(b) 'US24' steel.
Fig. 8.9: Extrapolation of measured lattice parameter against Nelson-Riley function (i.e., $\frac{\cos^2 \theta}{\sin \theta} + \frac{\cos^2 \theta}{\theta}$). $\theta$ is the diffraction angle.

(a) 'US3' steel.
(b) 'US24' steel.
Fig. 8.10: A plot of the maximum volume fraction of bainitic ferrite obtained in homogenised ‘US83’ steel, versus the corresponding volume fraction for as-received ‘US83’ steel. The line has a slope of unity and serves to illustrate that except at the transformation temperatures near $B_s$, the extent of transformation is larger in the homogenised samples.

Fig. 8.11: A plot of the maximum volume fraction of bainitic ferrite obtained in homogenised ‘US24’ steel, versus the corresponding volume fraction for as-received ‘US24’ steel. The line has a slope of unity and serves to illustrate that except at the transformation temperatures near $B_s$, the extent of transformation is larger in the homogenised samples.
Fig. 8.12a: Microanalysis data from the bainitic regions in a heterogeneous sample of 'US83' steel. The error bars indicate the typical 95% confidence statistical error and the average composition is in each case indicated by the dashed horizontal line.
Fig. 8.12b: Microanalysis data from the martensitic regions in a heterogeneous sample of 'US83' steel. The error bars indicate the typical 95% confidence statistical error and the average composition is in each case indicated by the dashed horizontal line.
Fig. 8.13a: Microanalysis data from the bainitic regions in a heterogeneous sample of 'US24' steel. The error bars indicate the typical 95% confidence statistical error and the average composition is in each case indicated by the dashed horizontal line.
Fig. 8.13b: Microanalysis data from the martensitic regions in a heterogeneous sample of 'US24' steel. The error bars indicate the typical 95% confidence statistical error and the average composition is in each case indicated by the dashed horizontal line.
Fig. 8.14: Bright field transmission electron micrograph showing upper bainite in a heterogeneous sample of ‘US83’ steel.

(a) Isothermally transformed to bainitic ferrite at 400 °C for approximately 90 minutes before quenching to ambient temperature.

(b) Isothermally transformed to bainitic ferrite at 420 °C for approximately 90 minutes before quenching to ambient temperature.
Fig. 8.15: Bright field transmission electron micrograph showing upper bainite in a heterogeneous sample of 'US24' steel.

(a) Isothermally transformed to bainitic ferrite at 400 °C for approximately 90 minutes before quenching to ambient temperature.

(b) Isothermally transformed to bainitic ferrite at 420 °C for approximately 90 minutes before quenching to ambient temperature.
Fig. 8.16: Calculated\cite{3,4} $T_0$, $A_{c3}'$ and $A_{e3}'$ phase boundaries for 'US83' steel. The experimental data are for samples transformed isothermally to bainitic ferrite and carbon enriched residual austenite at a variety of temperatures.

Fig. 8.17: Calculated\cite{3,4} $T_0$, $A_{c3}'$ and $A_{e3}'$ phase boundaries for 'US24' steel. The experimental data are for samples transformed isothermally to bainitic ferrite and carbon enriched residual austenite at a variety of temperatures.
Fig. 8.18: Results from the slice model calculations for as-received and homogenised samples of 'US83' steel. Points in the graph represent the experimental data.

(a) Calculations based on $T_0$ curve.

(b) Calculations based on $T'_0$ curve.
Fig. 8.19: Results from the slice model calculations for as-received and homogenised samples of 'US24' steel. Points in the graph represent the experimental data.
(a) Calculations based on $T_0$ curve.
(b) Calculations based on $T'_0$ curve.
Fig. 8.20: Graphs showing the differences in the volume fraction of bainite in the homogeneous and heterogeneous "US24" steel samples as a function of Mn concentration.

(a) The average Mn concentration was varied keeping the absolute range same.

(b) The Mn concentration range was varied keeping the minimum at a constant.
**Fig. 8.21:** Dilatometric curves showing the transformation to martensite in heterogeneous and homogeneous 'US83' steels, after the specimens were isothermally transformed to bainite at different temperatures, with enough time at each isothermal transformation temperature to ensure that bainitic ferrite formation stopped. Graphs (a), (c), (e), (g) and (i) are for homogeneous samples and (b), (d), (f), (h) and (j) are from heterogeneous samples.
Fig. 8.21: (continued .... )
Fig. 8.22: Thermodynamically calculated\(^{[7,8]}\) and experimentally determined \(M_s\) temperatures for homogenised and heterogeneous samples, after partial isothermal transformation to bainite.
Fig. 8.23: Comparison of the observed and calculated volume fractions of martensite. The calculations utilise the Koistinen and Marburger's equation\cite{9}. A common value of 0.004 was assigned to $C_1$ for all these calculations.

Fig. 8.24: Comparison of experimental results with those calculated by the new model based on equation 8.9.
Fig. 8.25: Comparison of the calculated and experimental maximum volume fractions of bainite and martensite in the "US3" steel. Data points marked with the same number are from the same heat treatment.

(a) Heterogeneous alloy.

(b) Homogeneous alloy.
REFERENCES

9.1 Summary

Phase transformations in different heterogeneous steels have been investigated using thermodynamic analysis and phase transformation theory, backed by experimental confirmation. It is found that the maximum volume fraction of bainite formed at any temperature (except above the $B_s$ of homogeneous alloy) is lower in samples containing chemical segregation when compared with corresponding homogeneous alloy. A model has been developed which explains the results quantitatively, as long as the carbon distribution in the austenite does not homogenise during the course of bainite transformation. That it does not do so has been confirmed, since the $M_s$ temperatures of partially bainitic specimen have been found to be much higher than expected. It has also been shown that if an opportunity is provided for carbon to distribute evenly throughout the residual austenite during the development of the bainitic microstructure, then the extent of transformation is always larger for the heterogeneous samples when compared with the homogenised samples. The later case was found to be more applicable in the formation of allotriomorphic ferrite in a heterogeneous alloy, where due to higher transformation temperatures involved carbon can distribute evenly throughout the residual austenite to facilitate still more transformation.

The major effect of chemical segregation on martensite transformation, in the steel studied, is to extend the range over which the reaction occurs relative to homogenised samples. It was also found that the presence of bainitic ferrite does not significantly alter the way in which the subsequent transformation to martensite occurs. All the data from homogeneous and heterogeneous samples have been rationalised using a new model of athermal martensite kinetics, which includes an effect of autocatalytic nucleation.

Reaustenitisation from a mixture of bainite and austenite, in homogeneous and heterogeneous samples has also been studied under isothermal conditions and in circumstances where the nucleation of austenite is not necessary. Dilatometric results can
be explained well by a published theory for reaustenitisation. As initially higher volume fractions of bainite were obtained in the homogeneous alloy its reaustenitisation start temperature will be lower than the heterogeneous alloy. The temperature at which the completion of reaustenitisation occurs, being dependent on average carbon content of the alloy should be the same for homogeneous and heterogeneous alloys.

9.2 Further Work

The present work has been on relatively higher Si content alloys, it will be interesting to study the effect of heterogeneities on the bainite reaction in alloys where carbide precipitation also accompanies ferrite formation. It will be worth checking for any correlation between banding and austenite grain structure. The existing model could be extended to investigate the phase transformations in heterogeneous austempered ductile cast irons which are becoming commercially important in automobile industry. Although this work is a part of a project into prediction of complete microstructure of steel weld deposits, all the experiments were done on wrought alloys. Some weld deposits should be tried and tested for this purpose. A study into a heterogeneous steel with an artificially modulated composition profile can help refine this model.

The model presented for the kinetics of martensitic transformation assumes that all the plates of martensite have identical volume. Moreover, it considers that all nucleation sites have the same activation energy. These approximations require much further research and characterisation.

This work needs to be related quantitatively to the influence of segregation on mechanical properties particularly as some qualitative and quantitative relationships can be found in the literature for homogeneous alloys.

More generally, it would be fascinating to investigate all the problems of heterogeneity using artificially modulated steels, in which not only the modulation wavelength but also its morphology can be controlled. The kinetics need to be developed further to treat the complete evolution of microstructure as a function of time, rather than just the maximum degrees of reaction obtained during isothermal reaction. In this respect, the experimental data accumulated here could be of considerable value in testing any overall transformation kinetics models for heterogeneous steels.
C Program for the analysis of bainitic transformation in heterogeneous Si containing steels. The steel is divided into slices of different compositions, C the maximum volume fraction of bainite, for a given transformation temperature C is then computed for each slice; taking care of nucleation (B1 temperature) C & growth (T0 limit). Slices transform independent of each other and the C carbons is not allowed to homogenise among the slices. The results averaged C and compared with a slice of the corresponding average composition. C This program calculates volume fraction of martensite also, Ms temperature is C calculated from the carbon content of residual austenite left after the C isothermallyformed bainite at any specific temperature in every slice C individually!!! C Typical data set follows:
C 673 (temperature in Kelvin) C 0.43 0.50 0.60 0.70 0.80 0.90 1.00 (Composition of slice 1 in wt.%)
C 0.43 0.60 0.60 0.70 0.80 0.90 1.00 (Composition of slice 2 in wt.%)
C C Si Mn Ni Mo Cr V
C

IMPLICIT REAL*8(A-H,K-Z), INTEGER(I)
DOUBLE PRECISION CR(8),DT0(150),DT0400(150)
& E(8),F(8),M(150),B(150),LA(150),XGAMMA(150),VOLF(150)
& CN(150),Si(150),Mn(150),N(150),Mo(V),V(150),Fe(150)
& CR(150),WXD(5),VG(150),CD(8),XC(150),VMF(150)
VINC=0.000005=00
ISTOP=0
AVSVOL=0.0
XMS=0.00
C1=0.0
C2=0.0
C3=0.0
C4=0.0
C5=0.0
C6=0.0
C7=0.0
READ5,*+KELVIN
T50=KELVIN-273.0
XALPHA=XALPHA+KELVIN
WRITE(6,9)KELVIN,XALPHA,VINC
DO 1 I=1,200
READ5,*+END=+2NL,C(1),C(2),C(3),C(4),C(5),C(6),C(7)
CN(I)=C(1)
SE(I)=C(2)
M(T)=C(3)
N(I)=C(4)
MO(I)=C(5)
CR(I)=C(6)
VD(I)=C(7)
FE(I)=1.0000+0.0(C(1)+C(2)+C(3)+C(4)+C(5)+C(6)+C(7))
C1=C1+C(1)
C2=C2+C(2)
C3=C3+C(3)
C4=C4+C(4)
C5=C5+C(5)
C6=C6+C(6)
C7=C7+C(7)
DO 43 II=1,7
E(I)=E(I)+II
43 CONTINUE
CALL TZERO,C,KELVIN,XD0(1),XD0400(1)
CALL MUGE65,B5(7)
XBAR=C1
WRITE(8,100)XD0(1),B5(7)
1 CONTINUE
0(1) = C1/SLICE
0(2) = C2/SLICE
0(3) = C3/SLICE
0(4) = C4/SLICE
0(5) = C5/SLICE
0(6) = C6/SLICE
0(7) = C7/SLICE
DO 70 J=1,7
WD(J) = D(J)
70 CONTINUE
DO 56 J=1,7
PJU(J) = D(J)
56 CONTINUE
CALL T2CR(1D, KELVIN, XTOH, XTOH0)
CALL MUQ(F, MS, BS)
WRITE(6,75) BS, XTOH
75 FORMAT(1B36, 10D16)
IF (BS .LT. 150) GOTO 789
GOTO 85
85 IF (XTOH .LT. 3710) GOTO 789
GOTO 789
789 VOLH = 0.0
GOTO 878
878 VOLH = XTOH - D(J)
GOTO 789
85 IF (XTOH .GT. XALPHA) GOTO 987
GOTO 789
987 VOLU = (XTOH - 0(J)) / (XTOH - XAUHA)
678 VGH = 1.0D+00 - VOLH
XOM = WD(J) + (VOLH * WD(J))
DO 242 IN = 1, 8
242 CONTINUE
CALL MUQFWD, MS, BS
D1(MSH .GE. 20.0) GOTO 564
GOTO 465
465 VMH = 0.0
GOTO 45
564 VMH = (D(MSH) - 0.005) * VGH
45 WRITE(6,151) VMH
WRITE(6,252) MSH
252 FORMAT(1B36, 10D16)
DO 6 I = 1, 10
6 CONTINUE
14 DO 12 J = 1, SLICE
12 VG(J) = 1.0D+00 - VOLF(J)
233 CONTINUE
10 VSH = 0.0
GOTO 3
9352 VOLF(J) = VOLF(J) + VINCR
XGAMMA(J) = XBAR + (VOLF(J) * XBAR - XALPHA)
& (3.0D+00 - VOLF(J))
GOTO 5
3 IA(J) = STOP + IA(J)
VOLF(J) = VOLF(J) - VINCR
IF (VOLF(J) .LE. 0.00) GOTO 115
GOTO 4
115 VOLF(J) = 0.0
XGAMMA(J) = XBAR
4 CONTINUE
6 CONTINUE
14 DO 12 J = 1, SLICE
VOL(J) = 1.0D+00 - VOLF(J)
C Recalling the original composition (wt%) for each slice.....

CD(1)=CN(J)
CD(2)=Si(J)
CD(3)=Mn(J)
CD(4)=P(J)
CD(5)=Cr(J)
CD(6)=V(J)
XG(J)=<D(I)+<V(100-D(I))>{LOO+<CD(I)}

C Getting new composition (wt%) of residual austenite in each slice
C for Ms calculation.....
RT=100.00+0.00*D(I)+(100.00-0.00*CD(I))
DO 262 ND=2,7
CD(ND)=CD(OV)RT

262 CONTINUE
CALL MUC(MS(J),BS)
IF (MS(J) .GE. 20.0) GOTO 468
GOTO 864
864 VMF(J)=0.00
GOTO 464
468 VMF(J)=(1.00+0.00*EXP(-0.0054*CD(I)-20.00-0.00)*G(J))*V(J)
464 WRITE(6,909)MS(J),VMF(J),VOLF(J),XGAMMA(J)
909 FORMAT(' J= ',D12.4, ' VMF= ',D12.4, ' Volf= ',D12.4
& XG= ',D12.4)
XGMS=XGMS+XGAMMA(J)
AVEVOL=AVEVOL+VOLF(J)
VMF=VMF+VMF(J)
AVMS=AVMS+MS(J)
12 CONTINUE
XGMS=XGMS/SLICE
AVEVOL=AVEVOL/SLICE
VMF=VMF/SLICE
AVMS=AVMS/SLICE
WRITE(6,166)XGMS
166 FORMAT(' Average carbon in residual austenite=',F8.3)
WRITE(6,13)AVEVOL
WRITE(6,239)AVMS
239 FORMAT(' Average MS temperature=',F8.3)
131 FORMAT(' Average volume fraction of MARTENSITE',
& in heterogeneous alloy=',F8.3)
151 FORMAT(' Maximum volume fraction of MARTENSITE in ',
& an alloy of average composition=',F8.3)
13 FORMAT(' Average volume fraction of transformation',
& in heterogeneous alloy=',F8.3)
9 FORMAT(' KELVIN=',F7.0,' XALPHA, mol. fraction=',D12.4
& VOL INCREMENT=',D12.4)
10 FORMAT(' Slice Number',J5, ' XTO ',D12.4,
& BS ',D12.4)
15 FORMAT(' Maximum volume fraction of bainitic ferrite in ',
& an alloy of average composition=',F8.3)
STOP
END

C Subroutine********MUtC************

SUBROUTINE MUC(C,M,S,B)
DOUBLE PRECISION XX,X,T,R,A,A1,A2,A3,A4,A5,A6,A7,A8,A9,A10,A11,A12,
T1,T2,T3,T4,T5,T6,T7,T8,T9,T10,T11,T12,T13,T14,T15,T16,T17,T18
INTEGER I,J,K,L,M,N,MON,BO1,BO2,BO3,BO4,BO5,BO6,BO7,BO8,BO9,BO10,
BO11,BO12,BO13,BO14,BO15,BO16,BO17,BO18,BO19,BO20,BO21,BO22,
BO23,BO24,BO25,BO26,BO27,BO28,BO29,BO30,BO31,BO32,BO33,BO34,
BO35,BO36,BO37,BO38,BO39,BO40,BO41,BO42,BO43,BO44,BO45,BO46,
BO47,BO48,BO49,BO50,BO51,BO52,BO53,BO54,BO55,BO56,BO57,BO58,
BO59,BO60,BO61,BO62,BO63,BO64,BO65,BO66,BO67,BO68,BO69,BO70,
BO71,BO72,BO73,BO74,BO75,BO76,BO77,BO78,BO79,BO80,BO81,BO82,
BO83,BO84,BO85,BO86,BO87,BO88,BO89,BO90,BO91,BO92,BO93,BO94,
BO95,BO96,BO97,BO98,BO99,BO100,BO101,BO102,BO103,BO104,BO105,
BO106,BO107,BO108,BO109,BO110,BO111,BO112,BO113,BO114,BO115,
BO116,BO117,BO118,BO119,BO120,BO121,BO122,BO123,BO124,BO125,
BO126,BO127,BO128,BO129,BO130,BO131,BO132,BO133,BO134,BO135,
BO136,BO137,BO138,BO139,BO140,BO141,BO142,BO143,BO144,BO145,
BO146,BO147,BO148,BO149,BO150,BO151,BO152,BO153,BO154,BO155,
BO156,BO157,BO158,BO159,BO160,BO161,BO162,BO163,BO164,BO165,
BO166,BO167,BO168,BO169,BO170,BO171,BO172,BO173,BO174,BO175,
BO176,BO177,BO178,BO179,BO180,BO181,BO182,BO183,BO184,BO185,
BO186,BO187,BO188,BO189,BO190,BO191,BO192,BO193,BO194,BO195,
BO196,BO197,BO198,BO199,BO200,BO201,BO202,BO203,BO204,BO205,
BO206,BO207,BO208,BO209,BO210,BO211,BO212,BO213,BO214,BO215,
BO216,BO217,BO218,BO219,BO220,BO221,BO222,BO223,BO224,BO225,
BO226,BO227,BO228,BO229,BO230,BO231,BO232,BO233,BO234,BO235,
BO236,BO237,BO238,BO239,BO240,BO241,BO242,BO243,BO244,BO245,
BO246,BO247,BO248,BO249,BO250,BO251,BO252,BO253,BO254,BO255,
BO256,BO257,BO258,BO259,BO260,BO261,BO262,BO263,BO264,BO265,
BO266,BO267,BO268,BO269,BO270,BO271,BO272,BO273,BO274,BO275,
BO276,BO277,BO278,BO279,BO280,BO281,BO282,BO283,BO284,BO285,
BO286,BO287,BO288,BO289,BO290,BO291,BO292,BO293,BO294,BO295,
BO296,BO297,BO298,BO299,BO300,BO301,BO302,BO303,BO304,BO305,
BO306,BO307,BO308,BO309,BO310,BO311,BO312,BO313,BO314,BO315,
C(1)=C(1)/12.0115
C(2)=C(2)/28.09
C(3)=C(3)/54.94
C(4)=C(4)/158.71
C(5)=C(5)/5.94
C(6)=C(6)/2.0
C(7)=C(7)/50.94
B1=C(1)+C(2)+C(3)+C(4)+C(5)+C(6)+C(7)+C(8)
DO 107 U=2,7
Y(U)=C(U)
107 CONTINUE
DO 106 U=1,7
C(U)=C(U)+B1
106 CONTINUE
B2=0.0
T0=Y(2)*3+Y(3)*2+Y(4)*12+Y(5)*9+Y(6)*6+Y(7)*12
T2=3*Y(2)-37.5*Y(3)-6*Y(4)+20*Y(5)-15*Y(6)-44*Y(7)
P(2)=2013.041+763.8167*C(2)-4580.87*C(2)**2+28006.63*C(2)**3
1+3.8646*0*C(2)**4-2.4233*0*C(2)**5+6.9547*0*C(2)**6
P(3)=2012.067-1764.095*C(3)+6287.52*C(3)**2-2167.96*C(3)**3
12.0193*C(3)**4*4.3.1716*C(3)**5+1.38835*C(3)**6
P(4)=2006.0071+2332.2624*C(4)-54915.32*C(4)**2+1.6216*0*C(4)**3
1-4.9968*0*C(4)**4+1.8838*0*C(4)**5-5.5531*0*C(4)**6
P(5)=2006.834-2997.314*C(5)-7906.61*C(5)**2+1.0338*0*C(5)**3
1-1.3306*C(5)**4-8.4111*D+0*C(5)**5+2.0826*0*C(5)**6
P(6)=2012.647-922.4655*C(6)+33697.8*C(6)**2-3.5068*0*C(6)**3
1-8.5678*0*C(6)**4+6.7483*D+0*C(6)**5+2.0837*D+0*C(6)**6
P(7)=2011.9966-6497.918*C(7)-54117.266*C(7)**2
1+250118.108*C(7)**3*5-4.1876*0*C(7)**4
DO 108 U=2,7
B3=B3+I'(U)*Y(U)
B2=B2+Y(U)
108 CONTINUE
IF(B2 .EQ. 0.0) GOTO 455
W=(B3/B2)**4.187
455 W=8054.0
456 FTO=1.0
X1=C(1)
X2=0.001
R=8.314.53
W1=8887.0
H=3895.0
S=13.48
XEQ=0.3
XTO=0.07
XT0400=0.06
X44=0.1
INCEPT=1.0D+00
C00R=1.0D+00
SLOPE=1.0D+00
C98=4.0
C99=0.0
WS=0.0
DO 9 T1=473,1173,20
C98=C98+1
J98=0
J99=0
XT0=XT0-0.0001
XT0400=XT0400-0.0001
X44=0.3*XEQ
T=T1
B' (T.J.E. 1000) GOTO 20
H1=105525
S1=43.3421
GOTO 19
20 H1=111918
S1=51.44
19 F=4ENERGY(T,Y,T1,T20)
A1=AI+DLOG(DI-3.5X(DI+3.5X)))+(DI-S1T)/(R1T)

AIFE=DLOG(I-X)

TEST=2RT*(AIFE-AIFE) -RT*(A1-A)

IF (DABS(TEST) > 10.0) GOTO 5

DAI=(3*X/(3-4*X)/(3X-2-4X))

DA2=0.5DI+(1221-18+18X+3221X)

DA2=4*(DA225(DI-3.5X)-(DI-3.5X)))

DA1=DA1+1DA2

DAIFE=DAIFE-(DI-3.5X)

ERROR=TEST(RT*(DAIFE-DA1))

IF (ERROR > X) GOTO 29

GOTO 30

ERROR = 0.3X

X<XERROR

GOTO 7

6

GMAX=RT*(AI-A)

DI=DQRT9.8*X((2S1+3)+SV+S1)*X1)

T4=T42323

IF (FTOE > 0.0) GOTO 22

FTO=FTO1(5,5,5X1,T,W,H1,S1,FJJ1)

GOTO 21

22

FTO = 0.0

21

DFTO=FTO1(5,5,5X1,T,W,H1,S1,FJJ1)

J4=J49+1

IF (DABS(DFTO) < 10.0) GOTO 450

G9=G91(5,5,5X1,T,W,H1,S1,FJJ1)

IF (J4 < 94.0) GOTO 450

GOTO 21

94

XTO=0.0000

450

FTO400=FTO1(5,5,5X1,T,W,H1,S1,FJJ1)+400.0

J99=J99+1

F999.GE. 9) GOTO 92

IF (DABS(FTO400) < 10.0) GOTO 92

G9400=G91(5,5,5X1,T,W,H1,S1,FJJ1)

GOTO 451

451

XTO400=0.0000

92

V1=XT0-XT0(XT0-0.0013)

V12=QQEQ-XT0(QQEQ-0.0013)

V13=QQX1-XT0(QQX1-0.0013)

V14=FFV12

V12=FFV11

V13=FFV13

SHEART=DDEXP(0.24428DESD+0683.31+12.7-0.135D+23D+20.0DLOG(T)

1-5.5DLOGABS(GMAX))

DSTP=DDEXP(0.603D+0683.31+12.7-0.190D+23D+20.0DLOG(T)

1-4.5DLOGABS(GMAX))

IF (V14.EQ. 0.0) GOTO 453

GOTO 454

453

SHEART=1D+20

454

DDFTO(CW)=FTO

DT4=CW>T4

9

CONTINUE

2444

C99=C98-1

CALL ANAL(CW,INCEPT, SLOPE, CORR, DT4, DDFTO)

BS<400.0-INCEPT)/SLOPE

MS<(112.0D+00-1056.0D+00X1+94.1D+00-INCEPT)/SLOPE

IF (WS > 0.5) GOTO 9996

GOTO 24

9996

BS = WS

24

CONTINUE

RETURN

END

C Subroutine********TZERO********************************************

SUBROUTINE TZERO(C,T,XTO,XTO400)
DOUBLE PRECISION X, XI, TJ, R, H, H1, S, SI, S1
INTEGER IU, IJ, 99, 98, 97, B5
DOUBLE PRECISION D1, IJ, T, H, C, B1, B2, T10, T20, XI, T4, C, B3, B7, B9, B11, B13, B15
C
C DOING BY ATOMIC WEIGHT
C
C(1)=C(1)/12.0115
C(2)=C(2)/211.09
C(3)=C(3)/54.94
C(4)=C(4)/58.71
C(5)=C(4)/58.71
C(6)=C(6)/52.0
C(7)=C(7)/50.94
B1=C(1)+C(2)+C(3)+C(4)+C(5)+C(6)+C(7)+C(8)
C(1)=C(1)/12.0115
C(2)=C(2)/211.09
C(3)=C(3)/54.94
C(4)=C(4)/58.71
C(5)=C(5)/115.94
C(6)=C(6)/52.0
C(7)=C(7)/50.94
B1=C(1)+C(2)+C(3)+C(4)+C(5)+C(6)+C(7)+C(8)
DO 107 U;1,7
Y(U)=C(U)/B1
107 CONTINUE
C CALCULATING MOLE FRACTIONS
DO 106 U;1,7
C(U)=C(U)/B1
106 CONTINUE
B2=0.0
T10=Y(2)*C(2)+Y(3)*C(3)+Y(4)*C(4)+Y(5)*C(5)+Y(6)*C(6)+Y(7)*C(7)
T20=3*Y(2)+2.7*Y(3)+6*Y(4)+26*Y(5)-19*Y(6)+44*Y(7)
P2(2)=2013.0341+763.8167*02)+45802.873*02)*2-28961.63*02)**3
1+3.8640+06*02)**4+2.4232*07*02)**5+6.9547*07*02)**6
P3(3)=2012.087-1764.095*03)+6287.52*03)**2+21647.96*03)**3
1+3.1716*07*03)**4+3.1716*07*03)**5+3.1716*07*03)**6
P4(4)=2006.8017+2330.2424*04)+54915.32*04)**2+1.6216*06*04)**3
1-2.4968*07*04)**4+1.8838*08*04)**5+5.5531*08*04)**6
P5(5)=2006.834-2997.314*05)-3506.61*05)**2+1.0332*06*05)**3
1-1.3306*07*05)**4+8.4111*08*05)**5+2.0826*08*05)**6
P6(6)=2012.367-2997.314*06)-3506.61*06)**2+1.0332*06*06)**3
1+3.8640+06*06)**4+2.4232*07*06)**5+6.9547*07*06)**6
P7(7)=2011.996-2473.91*07)-5411.7566*07)**2+1.6216*06*07)**3
1+2501.181055*07)**2+3.167650*06*07)**4
DO 108 U;2,7
B3=B3+Y(U)*T10
B2=B2+Y(U)
108 CONTINUE
IF( B2.EQ. 0.0) GOTO 455
W= <B3/B2)*4.187
455 W=0.04
B2=1.0
X1=C(1)
R=8.31432
W1=68570.0
C ENTHALPY OF CARBON IN AUSTENITE
H=0.38575
C ENTHALPY OF CARBON IN AUSTENITE
S=1.348
X0=0.04
X0=0.03
C=0
W=0.0
J9=0
J9=0.0
IF ( T .LE. 1000 ) GOTO 20
H1=0.55525
S1=45.34521
GOTO 19
20 H1=111918
S1=51.44
C DO FOR ALPHA_---GAMMA FOR PURE IRON
C DO FOR ALPHA--GAMMA FOR PURE IRON (ZENER)
19 F=E NERGY(T,T10,T20)
C SITE EXCLUSION PARAMETER
J=1.DEXP(W(R*T))
J1=1.0.DEXP(W1,R*RI))
T4=7.273
C Calling subroutine FTOI—
FTOI=FTO1(SX,T,W,W1,H1,S1,FJ,J1)
C Calling subroutine FTOI—
21 DFTO=FTO1(SX,T10,T,W,W1,H1,S1,FJ,J1)
J98=J901
IF (DABS(DFTO) .LE. 10.0) GOTO 450
C Calling subroutine OFTO—
OFTO=FTOI(H,S,xTO,T,W,WI,HI,S I)11)
IF (OABS(OFTO) .LE. 10.0) GOTO 60
C Calling subroutine OFTO—
OFTO=FTOI(H,S,xTO,T,W,WI,HI,S I)11)
XTO=XTO-OFTO/OF9
IF (XTO .LT. 0.0001) GOTO 94
GOTO 21
94 XTO=0.0000
C Calling subroutine of FTOI—
450 FTOO=FTO1(SX,XT0400,T,W,W1,H1,S1,FJ,J1)+400.0
J90=J901
IF (DABS(FTOO) .LE. 10.0) GOTO 92
C Calling subroutine G91—
G91=G9I(XTO,T,W,WI,HI,S I)11)
IF (OABS(G91) .LE. 10.0) GOTO 94
XTO=XTO-G91/G94
IF (XTO .LE. 0.0001) GOTO 95
GOTO 450
95 CONTINUE
RE11JR.'1
END
C Subroutine**********FTO1**********
DOUBLE PRECISION FUNCTION FTOI(H,S,x1,T,W,WI,HI,S I)11)
DOUBLE PRECISION RX,T,T60,ZE,N2,ZENER,W,W1,H1,S1,FJ,
JI,J1,J1,D11,J1,S
D=OSQRT(I-2 '(1 +2' J)'X .(1 +S' J)'X'X)
OII=DSQRT(9-6'X'(2'JI +3)+(9+16' JI)'X'X)
T60- T'(1-X)/(28080"X)
IF (T60 .GT. 1.0) GOTO IS
IF (T60 .GT. 0.25) GOTO 17
C ZENER ORDERING .
ZENI=O.2307+42.7974*T6G-233.8631·T60*T60+64S.4455·T60*T60
1-954.399S(T60"4)+ 7l1.809S·(T6O"3)-211.5136·(T6O" 2)
ZEN2=-2.6702+45.6337*T6G-225.3965·T60*T60*267.71
1-771.6466(T60"3)
1-771.6466(T60"4)+53S.177S'(T6O" 1)-15
1.381S'(T6O" '6)
GOTO 16
17 ZEN2=1
ZEN1=3.295
16 ZENER=((2EN2*X)"2)-(50898.56/(X-1))-ZEN1*%X"0.6623741
ZENER=ZENER+1.187
GOTO 13
18 ZENER=0
15 R=8.31432
FTOI=X'R "T'DLOG(X'X)+X'(H I-{H)-(S1-(5)
"T +4'WI-6'W)-R'T"X'X'OLOG((I-2'J)'X,'X)+R'T"X'X'OLOG((I-2'J)'X,'X)
1-R'T"X'X'OLOG((1-3'X)'X+1-3'X)'X')+R'T"X'X'OLOG((1-2'J)'X)
1''X'X'OLOG((1D1-5'X')X}(11D1-5'X')X)+R'T"X'X'OLOG((1-5'X')X)+R'T"X'X'OLOG((1-5'X')X)
RETURN
END
C Subroutine**********G91**********
DOUBLE PRECISION FUNCTION G9I(XTO,T,W,W1,H1,S1,FJ,J1)
DOUBLE PRECISION RX,T,O,T,W1,H1,FJ,J1,FD,FDI,DT3,
1DT6,DSZEN1,DSENZ2,ZEN3,V1,V2,V3,V4,V5,V6,V7,V8,V9,G1,
1DSZEN,DSZEN,DZEN8
R=8.31432
FD=DSQRT(1-2'(1-2'J)'XTO+(1-8'J)'XTO'XTO)
FD1=DSQRT(3-6'XTO'XTO+3'(9-16'J)'XTO'XTO)
239
DT6=DT6/DTS
IF (DT6 .GT. 1.0) GOTO 48
IF (DT6 .LT. 0.25) GOTO 47
DZEN1=0.2307+42.7974*DT6-233.8631*(DT6**2)+645.4485*(DT6**3)
1:954.399S*(DT6**4)+711.809S*(DT6**5)+211.5136*(DT6**6)
DZEN2=2.6702+45.6377*DT6-225.3965*(DT6**2)+567.7112*(DT6**3)
1:771.6466*(DT6**4)+538.1787*(DT6**5)+15.8184*(DT6**6)
GOTO 46
47 DZEN2=1
DZEN1=1.295
46 DZEN3=(DZEN2**XTO)**2+(5098.56*(1-XTO)+DZEN1**XTO)*
10*(0.6623741)
DZEN3=DZEN3**4.187
GOTO 45
48 DZEN3=0.0
45 V1=FD1+3*XTO
V2=FD1+3*XTO
V3=1-2*(1+1)*XTO-FD
V4=2*(XTO-1)
V5=FD1+3*XTO
V6=FD1+3*XTO
V7=XTO-2+4*XTO*(XTO-FD)
V8=XTO-6*(1+6*(1+1)*XTO)/FD1
V9=4*(1-0.5)/(1-0.5)**(0.6623741)
G1=2-DLOG(VXTO)**2=4-DLOG((1-XTO)**2)-10-DLOG(1-2*XTO)**(10)
1-DLOG(VV)**(6-6)*(XTO-V1)**((7+V1+V3-V2))
1-DLOG(VV)**(6-6)*(1-XTO)**((4*V1-V3)**(3))
1-DLOG(VV)**(6-6)*(XTO)**((4*V1-V3)**(3))
1/V3=V3+4.56.71+1.771.6466*(XTO**4)
1/V3=V3+4.56.71+1.771.6466*(XTO**4)
F=FD1+FD1+FD1+FD1
1-V1=V1-V2-V3-V4-V5-V6-V7-V8-V9-V10-V11
IF (DT6 .GT. 1.0) GOTO 90
DZEN3=(-3.3948+3.6112*DT6-1.3476*(DT6**2)+2.0869*
1-(1-XTO)**(2))
DZEN4=(-3.3118+1.5462*DT6-3.2449*(DT6**2)+2.0869*
1-(1-XTO)**(2))
DZEN8=5098.56*(DZEN2**XTO)**2+(1-XTO)**2+(5098.56**2)
1DZEN2**DZEN8**XTO**2+2*(XTO-DZEN2**XTO*(1-XTO))+DZEN1
1**(0.6623741)+DZEN7**XTO*(0.6623741)
GOTO 91
90 DZEN8=0.0
91 G91=V9+T1**G1+DZEN3-F
RETURN
END
C Subroutine************PPF**********
DOUBLE PRECISION FUNCTION PPF(V)
DOUBLE PRECISION V
IF (V .LE. 0.0) GOTO 1
IF (V .GT. 1.0) GOTO 1
2 GOTO 3
PPF=0.0
GOTO 4
3 PPF=V
4 RETURN
END
C Subroutine************ENERGY**********
DOUBLE PRECISION FUNCTION ENERGY(T,T10,T20)
DOUBLE PRECISION T,T10,T20,F,F
T=T+100*T20
IF (T .LT. 100) GOTO 1
IF (T .LT. 700) GOTO 2
IF (T .LT. 900) GOTO 3
F=F+1.099390-0.259576*(T-T1140)**2/F)
F=F+2.098030-6*(T-T1140)**(2)-3.85403-9*(T-T1140)**(4)
GOTO 4
1 F=1.38**T7-1499
GOTO 4
2 F=1.65786**T7-1.581
GOTO 4
3 F=1.3089**T7-1.331
ENERGY=(141*T10 + F)*4.187
RETURN
END
DOUBLE PRECISION FUNCTION XALPH(T)
DOUBLE PRECISION T,CTEMP
CTEMP=(T+273.0d+00)/900.0d+00
XALPH=0.15280d-02-0.8164d-02*CTEMP+0.2450d-01*CTEMP*CTEMP
&-0.0.8966d-02*CTEMP*CTEMP*CTEMP
RETURN
END
SUBROUTINE ANAL(C98,INCEPT,SLOPE,CORR,X,Y)
DOUBLE PRECISION AX,AX2,AY,AY2,AXY,INCEPT,SLOPE,
AX(40),Y(40)
INTEGER C98,J1
I=C98
C98=C98-10
AX=0.0d+00
AY=0.0d+00
AX2=0.0d+00
AY2=0.0d+00
AXY=0.0d+00
DO 1 1=1,C98
AX=AX+X(I)
AY=AY+Y(I)
AXY=AXY+X(I)*Y(I)
AX2=AX2+X(I)**2
AY2=AY2+Y(I)**2
1 CONTINUE
INCEPT=(AXY*AX2-AX*AXY)/(C98*AX2-AX*AX)
SLOPE=(C98*AXY-AX*AY)/(C98*AX2-AX*AX)
CORR=(C98*AXY-AX*AY)/(DSQRT((C98*AX2-AX*AX)**
&*(C98*AX2-AY*AY)))
C98=11
RETURN
END
APPENDIX 2

C Program for the analysis of bainitic transformation in heterogeneous Si containing steels. The steel is divided into slices of different compositions, the maximum volume fraction of bainite, for a given transformation temperature is then computed for each slice; taking care of nucleation (Bs temperature) & growth (To limit). The carbon is allowed to redistribute among the slices after each increment of transformation.

C The results averaged and compared with a steel of the corresponding average composition.

C Typical data set follows:
C 673 (temperature in Kelvin)
C 0.4 0.50 0.60 0.70 0.80 0.90 1.00 (Composition of slice 1 in w.%) 0.4 0.60 0.60 0.70 0.80 0.90 1.00 (Composition of slice 2 in w.%) 0.5 Si Mn Ni Mo Cr V

IMPLICIT REAL *(A-H,K-Z), INTEGER *(I)
DOUBLE PRECISION C(S),D(S),XTO(100),XT0400(100)
& E(S),F(S),MS(100),BS(100),LA(100),XGAMMA(100),VOLF(100)
& ,CN(100),SE(100),V1(100),SI(100),MOX(100),MO(100),FR(100)
& ,CR(100),WD(100),VG(100),CO(100),XG(100),VF(100)
VINCRC=0.00005D+00
IST0P=0
AVEVOL=0.0
C1=0.0
C2=0.0
C3=0.0
C4=0.0
C5=0.0
C6=0.0
C7=0.0
READ5,*,KELVIN
T50=KELVIN-273.0
XALPHA=XALPHA(KELVIN)
WRITE(6,4444)
4444 FORMAT('YOU ARE ALLOWING CARBON TO HOMOGENIZE!!! ')
WRITE(6,9,KELVIN,XALPHA,VINC)
DO 1 I=1,100
READ5,*,END=2(C11,C22,C33,C44,C55,C66,C77)
CN(I)=C11
SN(I)=C22
MN(I)=C33
NN(I)=C44
MM(I)=C55
CR(I)=C66
V(I)=C77
FE(I)=100.0D+0(C11+C22+C33+C44+C55+C66+C77)
C1=C1+C11
C2=C2+C22
C3=C3+C33
C4=C4+C44
C5=C5+C55
C6=C6+C66
C7=C7+C77
DO 43 IJ=1,7
EU(IJ)=C(UIJ)
43 CONTINUE
CALL TZERO(C,KELVIN,XTO(I),XT0400(I))
CALL MUC(E,BS(I))
XBAR=C(I)
WRITE(6,10,I,BS(I))
1 CONTINUE
2 ISLICE=1
D11=C1(ISLICE)
DO 70 JU=1,7
   J=JU
   IF (J .LT. TISO) GOTO 789
   GOTO 85
85   IF (XTO(J) LE. 0.0) GOTO 789
   GOTO 79
79   IF (XTO(J) .GT. XALPHA) GOTO 987
   GOTO 789
789  VOL(J)=0.0
   GOTO 678
987  VOL(J)=(XTO(J)-0.0)/(XTO(J)-XALPHA)
678  VGH=1.0D0+VOL(J)
   DO 101 JA=1,ISLICE
     XGAMMA(J)=D(J)
     VOLF(J)=0.0
   101 CONTINUE
   AVEX=0.0
   WRIT(6,15) VOLF(J)
   DO 6 1=1,10
     IF(ISTOP .EQ. ISLICE) GOTO 14
     DO 4 JEI=1,ISLICE
       IF (J=J(U) .EQ. I) GOTO 4
       IF (BS(J) LT. TISO) GOTO 5329
       GOTO 9352
5329  VOLF(J)=0.0
       GOTO 5
9352  VOLF(J)=VOLF(J) + VINC
       XGAMMA(J)=AVEX
       IF(XGAMMA(J).GE. XTO(J)) GOTO 5
       GOTO 4
5   IA(J)=1
     ISTOP=ISTOP+1A(J)
     VOLF(J)=VOLF(J)+VINC
     IF (VOLF(J) .LT. 0.00) GOTO 115
     GOTO 4
115  VOL(J)=0.0
       XGAMMA(J)=AVEX
4   CONTINUE
   AVEVOL=0.0D0+00
   DO 90 J33=1,ISLICE
     AVEVOL=AVEVOL+VOLF(J33)
90   CONTINUE
   AVEVOL=AVEVOL/ISLICE
   AVEX=D(I)+AVEVOL*(XALPHA-I/I.0D0)=AVEVOL
6   CONTINUE
14   AVEVOL=0.0
     DO 12 JA=1,ISLICE
       AVEVOL=AVEVOL+VOLF(J)
12   CONTINUE
   XGMS=XGMS/ISLICE
   AVEVOL=AVEVOL/ISLICE
   WRITE(6,166)XGMS
166   WRITE(6,13)AVEVOL

13 FORMAT(' Average volume fraction of transformation', 
& in heterogeneous alloy = 'F8.3')
9 FORMAT( 'KELVIN = ' , 'F7.0', 'XALPHA, mol. fraction = ' , 'F12.4 
& VOL INCREMENT = ' , 'F12.4)
10 FORMAT(' Slice Number ' , 'F3', 'XTO ' , 'F12.4, 
& BS ' , 'F12.4')
15 FORMAT(' Maximum volume fraction of bainitic ferrite in ' , 
& an alloy of average composition = 'F8.3')
STOP
END
C Subroutine**********MUC**************
SUBROUTINE MUC(M,C,MS,BS)
DOBLE PRECISION X(1,T,R,A,A1,AFE,AFE1,DA1,DA2,DA1FE,JB1,J1,5,51
INTEGER T1,NO,C100,U,B4,B5,B9,B9,CD9,C99
DOUBLE PRECISION D11,F10,FT0400,CD400,CH12,DF12, 
1D44,AFE44,DA44,DA44,DF44,DF44,DF44,DF44,DF44,DF44,DF44,DF44, 
1V13,1V14,99,1V19,1V12,XT,DF0,INCEPT,XI,ALPHA,CORR, 
1DEQ,ETEQ,T10,T20.XA,AFEQ,AEQ,ETEQQ,TEQ, 
1JI,1D,D1,W1,F1,TEST,CMAX,ERROR,T4,XI,Q,PSON,JPR0 
1,C(8),B1,B2,B7,P(Y),B7,B3,B5,W5,W5,MS
C100=1
DO 24 I=1,C100,1
B5=111
B3=O
C(I)=(100.0-C(1)-C(2)-C(3)-C(4)-C(5)-C(6)-C(7))/55.84
C(1)=C(1)/10.0115
C(2)=C(2)/28.09
C(3)=C(3)/50.94
C(4)=C(4)/56.71
C(5)=C(5)/67.94
C(6)=C(6)/52.50
C(7)=C(7)/50.94
B1=-(C(1)+C(2)+C(3)+C(4)+C(5)+C(6)+C(7))/C(8)
DO 107 U=1,7
Y(U)=C(U)/C(8)
107 CONTINUE
DO 106 U=1,7
B2=O
B3=O
106 CONTINUE
B3=O
T10=Y(2)*(-3)+Y(3)*2+Y(4)*12+Y(5)*(-9)+Y(6)*(-1)+Y(7)*(-12)
T20=3*Y(2)-37.5*Y(2)+6*Y(4)-26*Y(5)+19*Y(6)-44*Y(7)
PT0=201.524+783.617*CT2+650.200*CT2+2.2800*63*CT2**3
1+0.3640*66*CT2**4+2.44233*67*CT2**5+6.93470*67*CT2**6
PT0=201.2067+1754.005*CT2+267.52*CT2**2+2.01647*66*CT2**3
1.20.0119D0+66*CT2**4+3.1717D0+70*CT2**5+5.1388D0+80*CT2**6
P40=200.63817+2350.2424*CT4+549.1932*CT4+2.61216D0+66*CT4**3
1-2.4967D0+70*CT4**4+1.8838D0+66*CT4**5+5.5533D0+80*CT4**6
P50=200.6384-2997.314*CT5-7906.61*CT5**2+2.0328D0+66*CT5**3
1-2.3500D0+70*CT5**4+4.8411D0+70*CT5**5+2.0800D0+80*CT5**6
P60=201.2387-922.8365*CT6-356.3836*CT6+2.566827.35*CT6**3
1-8.5767D0+66*CT6**4+4.57482D0+70*CT6**5+2.0837D0+80*CT6**6
P70=201.9996-6247.3118*CT7-541.7256*CT7**2
1+2501.18.1063*CT7**3+4.1627D0+66*CT7**4
DO 108 U=2,7
B3=-(U-1)*Y(U)
108 CONTINUE
IF(UQ.EQ.0) GOTO 455
B3=+U*Y(U)
108 CONTINUE
IF(B3.EQ.0) GOTO 455
W=A(B3)/B2*A.187
GOTO 456
455 W=A8544.0
GOTO 456
456 FTO=1.0
X1=C(1)
XA=0.001
R0=31.452
W1=4577.0
H=38575.0
S=13.48

244
DO 9 n=473,1173,20
C98=C98+1
198=0
199=0
XTO=XTO+0.0001
XT0400=XT0400+0.0001
X44=0.3*XEQ
T=T
IF (T .LE. 1000) GOTO 20
H1=105525
S1=15.3431
GOTO 19
20 H1=1111918
S1=54.44
19 F=ENERGY(T,T1,T2)
J=1-DEXP(W(R*T))
51 DEQ=D*SQRT((1-2*T1)*XEQ+(1-8*T1)*XEQ*XEQ)
TEQ=5*DLOG([1-XEQ]/[1-XEQ])
TEQ=TEQ-DEQ+T-P
IF (DABS(TEQ) .LT. 1.0) GOTO 50
ETEQ=5*(1-XEQ)/[1-XEQ]
ETEQ=ETEQ+DEQ+T-P
XEQ=TEQ
GOTO 51
50 ASEQ=5*DLOG((1-2*XEQ)/XEQ)+6*W(R*T)+15*(T1)/(R*T)
AEQ=AEQ+DLOG((D-I+3*XI)/(D+I)*XI)**6
AFEQ=5*DLOG((I-XI)/(1-2*XI)+DLOG((I-2*XI)+(4*I+1)*XI)**6)
IF (XI .LT. XI) GOTO 2443
GOTO 2444
2443 IF (WS .EQ. 0.0) GOTO 2441
GOTO 2444
2441 WS=T4
GOTO 2444
2442 D=D*SQRT((1-2*I)*XI+(1-I)*XI)**6
A=4*W(R*T)+DLOG((I-3*XI)+(I-2*XI))**6
A=A+5*DLOG((1-2*XI)+(1-8*XI)*X1)**6
A=A+(I-5.5*I)*R*T
AEF=5*DLOG((I-X1)+(1-X1))**6
AEF=AEF+DLOG((I-2*I)+(4*I+1)*XI)/[1+I]*XI)**6
FSON=R**T*X1+AEF-A*(1-X1)**6
PR2=8*R**T*(AEF-A)*I/0.315
103 D44=D*SQRT((I-2*I)*X44+(1-I)*X44)**6
D44=6*W(R*T)+2*244+16*I*X44
A44=5*DLOG((I-2*X44)**6)
A44=A44+DLOG((I-2*X44)+6*W(R*T)+5.5)**6
103 D44=5*DLOG((I-2*X44)+(5)**6)
F44=R**T*X44*(AEF-A)+(I-X44)**6
245
F44=F44-V14
IF (DABS(F44) .GE. 10.0) GOTO 101
GOTO 102
101 DA44=((5(1-2*X44)+5(X44)+6*(DD44+3))/(DD44+1)+3\*X44)
12(DD44+3)/(DD44+1-2\*X44)
DAFE44=((1-2*X44)-5(1-X44)+6*(4*X44-1)-2\*X44)+4*
15-1)/(X44-DA44-2*(X44-DA44-1))
DF44=RT(TAEQ-X44*DAFE44+X44*DAFEG44-444+AFE44)
X44=X44-F44/DF44
GOTO 103
105 X44=0.0
IF (C97 .GT. 0) GOTO 102
C97=1
WS=T4
GOTO 102
452 X44=99999999999.99999
IF(C97 .GT. 2) GOTO 9990
C97=3
WSI=T4
9990 WSZT4
GOTO 21
102 FPROA=FPRO+((XEQ-XA)J(XEQ-XI»)
X=0.00000X
J1=1-DEXP(-WI/(R+T»
7 D1=DSQRT(9-6\*X+(2\*Jl+3)+(9+16\*X)\*X)\*X)
A1=3*DELLOG(3-4\*X)\*X-2\*W1\*R\*T)
A1=A1+DELLOG((1-3+5\*X)(1+3-5\*X))*a+(11-51\*T))R\*T)
AIFE=DELLOG(1-X)
TEST=RT*(AIFE-AFE) -R*T*(A1-A)
IF (DABS(TEST) .GT. 10.0) GOTO 5
GOTO 6
5 DA1=(3-4\*X)\*X(4\*X)+(4\*X+4\*X+4\*X+4\*X)
DAe=0.001\*12/(1-18+18\*X-32\*X-32\*X)
DAe=4.((DA2+5)(1+3-5\*X)(1-3+5\*X))
DA1=DA1+DA2
DAIFE=1(X-1)
ERROR=TEST(R\*T*(DAIFE-DA1))
IF (ERROR .GT. X) GOTO 30
GOTO 29
30 ERROR =0.3\*X
29 X=X-ERROR
GOTO 7
6 GMAX=R\*T*(A1-A)
D11=DSQRT(5-6\*X1\*X2)+3)+9+16\*X1\*X1\*X11
T4=T-273
IF (FTO .GE. 0.0) GOTO 22
FTO=FTO\*(H,S,XTO,T,W,WI,HI,SI,FJ,JJ)
GOTO 21
22 FTO =0.0
21 DFTO=FTO((LS,XTO,T,W,W1,HI,SI,FJ,JJ))
J98=J98+1
IF (DFTO .GT. 1.0) GOTO 450
G9=O91(XTO,T,W,W1,HI,SI,FJ,JJ)
IF (J98 .GE. 9) GOTO 450
XTO=XT0-DFTO\*G0
IF (XTO .LE. 0.0001) GOTO 94
GOTO 21
94 XTO=0.0000
450 FTO040=FTO((LS,XTO040,T,W,W1,HI,SI,FJ,JJ))=400.0
J99=J99+1
IF99 .GE. 9) GOTO 92
IF (FTO040 .GT. 1.0) GOTO 92
G94=O91(XTO040,T,W,W1,HI,SI,FJ,JJ)
XT0040=XTO040-FTO040\*G9400
IF (XT0040 .LE. 0.0001) GOTO 451
GOTO 450
451 XTO040=0.0000
92 V11=XT0-X1\*(XTO-0.0013)
V12=XT0-XT0-X1\*XTO-0.0013)
V13=XT0-X1\*(X44-0.0013)
VII=FFF(V11)
V12=FFF(V12)
V13=FFF(V13)
SHEART=DEXP(0.343*62+0(3.1432*7)+0.1353+20+0.912*60+20+0.912*60+20)
1.9*2LOG(DABS(GMAX))
DFF=DEXP(0.601*62+0(3.1432*7)+0.1903+20+0.912*60+20)
IF (X44 EQ. 0.0) GOTO 453
GOTO 454

9 CONTINUE

2444 C98=C98-1
CALL ANAL(C98,INCEP,SLOPE,DIRF,DT4,DDFT0)
BS<4.00D-INCEP)/SLOPE
MS<1.120D-00-1058D-00+0*X1+94.1D-00-INCEP)/SLOPE
IF (WS LT. BS) GOTO 9996
GOTO 24

9996 BS=WS
24 CONTINUE
RETURN
END

C Subroutine**********TZERO*******************************
SUBROUTINE TZERO(C,T,XTO,XTO400)
DOUBLE PRECISION X,XI,T,R,H,HI,S,S1
INTEGER U,V,B4)99,C98,C97,B5
DOUBLE PRECISION DII,TRO,TRO400,XT0400,G9400,G9,XTO,DDFT0,T10,T20,
B3=0
C(S)=(I OO.Q..((I)-C(2)-<:(3 )-C(4 )-C(5)-(((6}(CT))lS5.84
C(1)=C(1)/12.0115
C(2)=C(2)/28.09
C(3)=C(3)/54.94
C(4)=C(4)/58.71
C(5)=C(5)/85.94
C(6)=C(6)/52.0
C(7)=C(7)/50.94
B1=C(1)+C(2)+C(3)+C(4)+C(5)+C(6)+((7)+((S)
DO 1<77U=2,7
Y(U)=C(UVC(S)
1<77 CONTINUE
C CALCULATING MOLE FRACTIONS.................................
DO 106 U=1,7
C(U)=C(U)/B1
106 CONTINUE
B2=0.0
T10=Y(2)*C(3)+Y(3)*C(4)+Y(4)*C(5)+Y(5)*C(6)+Y(6)*C(7)+Y(7)*C(8)
T20=Y(2)*C(3)+Y(3)*C(4)+Y(4)*C(5)+Y(5)*C(6)+Y(6)*C(7)+Y(7)*C(8)
PC=2021.3541+763.1676*C12+4382.87*C12)+2-283006.63*C12)**3
1.3.866G-06*CSS)**4-2.4233D-07*CSS)**5-6.857G-07*CSS)**6
PC=2021.3561-1646.0915*C12)+6287.52*C12)**5-2.2167.96*C12)**6
12.0119G-06*C12)**4+3.317G-07*C12)**5+1.388G-08*C12)**6
PC=2021.3581+2330.2434*C12)+54915.32*C12)**2+1.6216D-06*C12)**3
1.2.4968D-07*C12)**4+1.883D-08*C12)**5+5.531D-08*C12)**6
PC=2021.3564+2997.214*C12)+37066.61*C12)**2+1.0328D-06*C12)**3
1.1.3000D-07*C12)**4+8.411D-07*C12)**5+2.202D-08*C12)**6
PC=2021.3551+232.6255*C12)+33667.83*C12)**2+5.56827.85*C12)**3
1+8.567G-06*C12)**4+6.7682D-07*C12)**5+2.083T0D-08*C12)**6
PC=2021.3996-647.9114*C12)+541.7566*C12)**2
1+25011.1085*C12)**3+3.4.1676D+06*C12)**4
DO 108 U=2,7
B3=B3+P(U)*Y(U)
B2=B2+Y(U)
108 CONTINUE
IF(Y2 EQ. 0.0) GOTO 455
W=B3/B2**4.187
455 W=0.045
FTO=-1.0
X1=C(I)
R=8.31432
W1=45570.0

C ENTHALPY OF CARBON IN AUSTENITE

H=38575.0
C ENTROPY OF CARBON IN AUSTENITE

S=13.48
XTO=0.04
XT0400=0.03
G=0
D=0
W=0.10
J8=0
J99=0

IF (T LE. 1000) GOTO 20
H1=105525
S1=153421
GOTO 19

20 H1=111918
S1=51.44

C Calling subroutine ENERGY

C Calling subroutine FTO1

IF (DABS(DT0) LE. 10.0) GOTO 450

C Calling subroutine G91

C Calling subroutine FTO1

IF (DABS(DT0) LE. 10.0) GOTO 450

C Calling subroutine G91

C Calling subroutine FTO1

450 FT0400=FTO1(H,S,xT0,T,W,W1,HI,S1,F,J)
J99=J99+1
IF (J99 .GE. 10) GOTO 92

C Calling subroutine G9400

XTO400=XT0400-FT0400/G9400
IF (XTO400 LE. 0.0001) GOTO 451
GOTO 450

451 XTO400=0.0000

92 CONTINUE
RETURN

C Subroutine:

DOUBLE PRECISION FTO1(H,S,x,T,W,W1,HI,S1,F,J)
DOUBLE PRECISION R,X,T,T60,ZEN1,ZEN2,ZENER,W1,H1,S1,F,
J1,J2,J3,D,DISQRT(1-2*(I+2*J)*X+(-1+6*J)*X*X)
D=DISQRT(1-2*(I+2*J)*X+(-1+6*J)*X*X)
T60=T60*(X308900)
IF (T60 .GT. 0.0) GOTO 18
IF (T60 .GT. 0.0) GOTO 17
C ZENER ORDERING

ZEN1=0.2307+4.7974*T60-233.8631*T60*T60+645.4483*T60*T60*T60
1.954.3995*T60*4+711.8093*T60*5-211.5136*T60*6

248
ZEN2=-2.6702+4S.6337"1"60-22S.396S'TOO'T60+S67.7112'(TOO"3)
I-771.6466'(T60"4)+ S38.177S'(T60" '5)-ISI.381S'(T60" '6)
GOTO 16

ZEN2=1
ZEN1=3.295

ZEN3=0.0

R=8.31432
F01=X'R-'*DLOG(XTO)'X)'X*'I-DT6(5I-5)
1)*'T+'W1-4'W)+R'T(1-X)*DLOG(1-X)**4)+R'T(1-2*X)*DLOG(1-2*X)
1-R'TX)*DLOG((D-1+3*X)(1-3*X))''6)-R'TX)*DLOG((1-2*X)**4(4
1-1)(1)(2)`(2X)'(1)+)'6)+3*R'TX)*DLOG(3-4*X)+R'T
1*X*DLOG((D-1-3*X)(D1+3-5*X)**4)+(1-3)*Y*FZENER
RETURN
END

C Subroutine********G91***************
DOUBLE PRECISION FUNCTION G91(XTO,T,W,WI,HI,SI,F))I)
DOUBLE PRECISION R,XTO,T,W,WI,HI,SI,F))I,FD,FDI,DTS, DT6,DZE.'16,DZE.'17,DZE.'18
R=8.31432
FD=DSQRT(I-2'(1 +2'J)'XTO+(1 +8'1)'XTO'XTO)
FDI=DSQRT(9-6'XTO'(2' JI+3)+(9+16' Jl )'XTO'XTO)
DTS=28080'XTO/(I-XTO)
DT6=TDTS
IF (DT6 .GT. 1.0) GOTO 48
IF (DT6 .LT. 0.25) OOTO 47
DZENI =0.2307+42.7974'DT6-233.8631 '(DT6' '2)+645.4485'(DT6"3)
I-954.3995'(DT6' '4 )+S38.177S'(DT6" 5)-ISI.381S'(DT6' '6)
DZEN2= -2.6702+4S.6337"1"60-22S.396S'TOO'T60+S67.7112'(TOO"3)
I-771.6466'(T60"4)+ S38.177S'(T60" '5)-ISI.381S'(T60" '6)
GOTO 46

47 DZEN2=1
DZEN1=3.295

46 DZEN3=(DZEN2*XTO)**2*(5089.56)(1-XTO)+DZEN1'T*XTO*4(1.6623741)
GOTO 45
DZEN3=DZEN3+4.187
GOTO 46

48 DZEN3=0.0

45 V4=FD-1*3'XTO
V2=DF+1*3'XTO
V3=V4+4'2'-1*XTO-FD
V4=V2+3'2'(3*XTO)
V5=V4-3*5'XTO
V6=DF-3*5'XTO
V7=V5-1*3'XTO*J'TD
V4'P'=XTO-9.4'V1+16.6'J1*XTO*FD1
V4=HI-DO-(5I-5)*T-9*W'+4'W1
G1=DLOG(XTO)**2)+4'DLOG((1-XTO)**2)=10-DLOG((1-2*XTO)**10)
1-DLOG(V1/V2)*6'4'4'(XTO/V1)'/V1)+3-4'V2(2
1-DLOG(VX4/V4)**2)+4'(XTO/V3)**2)+4'(1-3*XTO)**2)+4'(1-V5*V4)/V7
1+3*DLOG(3-4*XTO)**4+DLOG(V5/V6)**4)-4'4'XTO
V1/3'V8=5'V5/V6)'V5
IF (DT6 .GT. 1.0) GOTO 90
DZEN4=3.948+13.6112'UP6-13.4378*(DTS**2)+(28080*DTS**2)*T(28080)
I(1-XTO)**2)
DZEN7=4'(3.318+15.7462'IT6-23.2449*(DTS**2)=T(28080)
I(1-XTO)**2)
DZEN8=5089.56(DZEN2*XTO)**2)(1-XTO)**2)+5089.56(2*
DZEN2*DZEN4*XTO**2)+2*XTO*DZEN2*XTO)(1-XTO)+DZEN1
1'T*XTO=6.6623741+DZEN1'T*XTO*0.6623741
GOTO 91

90 DZEN8=0.0

91 G91=V1-R'T*G1+DZEN8-F
RETURN
END

C Subroutine**********G91***************
DOUBLE PRECISION FUNCTION FFF(V)
DOUBLE PRECISION V
IF (V .LE. 0.0) GOTO 1
IF (V .GT. 1.0) GOTO 1
2 GOTO 3
1 FFF=0.0
GOTO 4
3 FFF=V
4 RETURN

C Subroutine********ENERGY*******************
DOUBLE PRECISION FUNCTION ENERGY(T,T10,T20)
DOUBLE PRECISION T,T10,T20,F,n
1 n=T*T10*T20
IF (17 .LT. 300) GOTO I
IF (17 .LT. 700) GOTO 2
IF (17 .LT. 940) GOTO 3
F=8.88909+0.26551·(17-1140)-1.049230.3·(17-1140)· ·2)
F=+2. 70013D-6·(17-1140)·3.58434D-9·(17-1140)·2)
GOTO 4
1 F=1.38*17-1499
GOTO 4
2 F=1.65186*17-1581
GOTO 4
3 F=1.50895*17-1331
4 ENERGY=141*17+ F*4.187
RETURN

DOUBLE PRECISION FUNCTION XALPH(T)
DOUBLE PRECISION T,CTEMP
CTEMP=T-273.2D+00/273.15D+00
XALPH=0.1529D-02-0.8816D-02·CTEMP+0.2450D-01·CTEMP·CTEMP
&-0.3470D-01·CTEMP·CTEMP·CTEMP
&+0.6966D-02·CTEMP·CTEMP·CTEMP·CTEMP
RETURN

SUBROUTINE ANAL(C98,INCEPT,SLOPE,CORR,X,Y)
DOUBLE PRECISION AX,AX2,AY,AY2,AXY,C98,INCEPT,SLOPE,CORR,X,Y
INTEGER C98,II
II=C98
C98=C98-10
AX=0.0D+00
AY=0.0D+00
AX2=0.0D+00
AY2=0.0D+00
AXY=0.0D+00
DO 1 i=1,C98
AX=AX+X(I)
AY=AY+Y(I)
1 AXY=AXY+X(I)*Y(I)
AX2=AX2+X(I)*X(I)
AY2=AY2+Y(I)*Y(I)
AY2=AY2+Y(I)*Y(I)
1 CONTINUE
INCEPT=(AY*AX2-AXY*AY)/C98*AX2-AXY*AX)
SLOPE=(C98*AXY-AY*AY)/DSQRT(C98*AX2-AX*AX)
CORR=(C98*AXY-AY*AY)/DSQRT((C98*AX2-AX*AX)*
& (C98*AY2-AY*AY))
C98=II
RETURN
END
The motion of austenite/ferrite interface is considered to be parallel to the local concentration planes. The steel is divided into slices of different compositions, $A_e3$ temperature of each slice is calculated and transformation is allowed only in slices whose $A_e3$ temperature is higher than the concerned transformation temperature. The extent of transformation is limited by pseudo-equilibrium mechanism. The carbon is permitted to redistribute among the slices after each increment of transformation. The results are averaged and compared with a slice of the corresponding average composition. Typical data set follows:

<table>
<thead>
<tr>
<th>Temperature (Kelvin)</th>
<th>Composition of slice 1 (wt.%)</th>
<th>Composition of slice 2 (wt.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>673</td>
<td>0.43 0.50 0.60 0.70 0.80 0.90 1.00</td>
<td>0.43 0.60 0.60 0.70 0.80 0.90 1.00</td>
</tr>
</tbody>
</table>

```
IMPLICIT REAL*(A-H,L-Z), INTEGER(I)
DOUBLE PRECISION C(8), D(8), XEQ(200)
&:, E(8), I'(8), MS(100), IN(100), GAMMA(200), VOLF(200)
&:, CN(200), SI(200), MN(200), Ni(200), Mo(200), V(200), Fe(200)
&:, CR(200), WD(6), VG(200), CD(6), XG(200), TA(3)(200)
&:, XEX(4), TVOLF, AVEVOL, MOMENT, TISO
VINCR=0.00005; ISTOP=0
AVEVOL=0.0D+0
TVOLF=0.0D+0
C1=0.0
C2=0.0
C3=0.0
C4=0.0
C5=0.0
C6=0.0
C7=0.0
READ5,*KELVIN
TISO=KELVIN-273.0D+0
XALPHA=XALPHA(KELVIN)
WRITE(6,4444)
4444 FORMAT(***CARBON IS ALLOWED TO DIFFUSE!!!************)
WRITE(6),XKELVIN,XALPHA,VINCR
WRITE(6),*9090
9090 FORMAT(------)
```

DO 1 I=1,101
READ5,*END=2(C(1),C(2),C(3),C(4),C(5),C(6),C(7)
C(1)=C(1)+C(2)+C(3)+C(4)+C(5)+C(6)+C(7)
DO 43 U=1,7
E(U1)=C(U1)
43 CONTINUE
CALL XEQ(QKELVIN(CXEQ(U))
CALL TEMP9X(TAE3(U))
XBAR=C(1)
WRITE(6,10)XEQ(U),TAE3(U)
WRITE(6,161)
161 FORMAT(**************)

1 CONTINUE
2 ISLICE=4-1
WRITE(4,'()') ISLICE
X(I)=C(ISLICE)
X(2)=C(ISLICE)
X(3)=C(ISLICE)
X(4)=C(ISLICE)
X(5)=C(ISLICE)
X(6)=C(ISLICE)
X(7)=C(ISLICE)
DO 70 J=1,7
WD(J)=D(J)
70 CONTINUE
DO 56 J=1,7
F(J)=D(J)
56 CONTINUE
CALL XEQ3(KELVIN,CXEQ(U))
CALL TE.W'3(F,TAE3(U))
WRITE(6,75)TAE3(U)
75 FORMAT(' k3H= '.010.4)
WRITE(4,'()')D(I)
IF (TABH LT. TISO) GOTO 789
GOTO 85
85 IF (XEQH < 0.0) GOTO 789
GOTO 79
79 IF (XEQH .GT. XALPHA) GOTO 987
GOTO 789
789 V0H=0.00
GOTO 678
987 V0H=V0H+XEQH-D(I)
GOTO 5
678 VG0H=V0H
WRITE(6,15)VG0H
DO 1020 I=1,ISLICE
XMA(I)=D(I)
V0L(I)=0.00+0.0
1020 CONTINUE
AVEVOL=V0L(I)
DO 6 I=1,ISLICE
IF (ISTOP .EQ. ISLICE) GOTO 14
DO 4 J=I,ISLICE
IF (IA(J) .EQ. I) GOTO 4
IF (TAB(J) LT. TISO) GOTO 133
GOTO 9352
133 VOL(J)=0.00+0.0
XMA(J)=AVEV
4 CONTINUE
AVEVOL=AVEV
DO 90 J=1,ISLICE
AVEVOL=AVEV+VOL(J)
90 CONTINUE
AVEVOL=AVEVOL
252
CONTINUE

AVEVOL=AVEVOL*SLICE

AVEEX=(AVEVOL*SLICE-XALPHA/2)*(1.0D+0-AVEVOL)

CONTINUE

AVEVOL=AVEVOL+VOLFU

WRITE(6,786)J,F,ID,AMMAU,XEQ,J1,AVEVOL

POR: SLICE='J3', VOLF='D10.3', XALPHA='D10.3', XEQ='D10.3', AVEVOL='D10.3'

CONTINUE

AVEVOL=AVEVOL*SLICE

WRITE(6,786)J,F,ID,AMMAU,XEQ,J1,AVEVOL

FORMAT(4X,6E15.3)

FORMAT(4X,6E15.3)

6 CONTINUE

10 CONTINUE

3 FORMAT(4X,6E15.3)

10 CONTINUE

3 FORMAT(4X,6E15.3)

10 CONTINUE
CONTINUE
IF(B2 .EQ. 0.0) GOTO 455
W=(B3/82) "4.187
GOTO 456
455 W=8054.0
456 CONTINUE
X1=C(1)
R=8.31432
W1=48570.0
I=3857.0
S=13.48
II=873
II2=1173
II3=15
II=0
201 XEQ=0.1
INCEPT=1.0D+00
SLOPE=1.0D+00
C98=0
C97=0
DO 9 TI=II2,II3
C98=C98+1
T=T1
IF (TI .GE. 1000) GOTO 20
H1=105128
$1=45.5425$1.
GOTO 19
20 H1=111918
$1=51.44
19 P=EENERGY(T1,T10,T20)
J=1-DEXP(-W/(R*T))
51 DEQ=D5QRT(1-2**J)*XEQ-(1+*J)*XEQ*XEQ
TEQ=P*LOG(XEQ)
TEQ=TEQ-DLOG(1-2*XEQ)
TEQ=TEQ*(1+2*XEQ)-1)
IF (DABS(TEQ) LT. 1.0) GOTO 50
ETEQ=ETEQ+ETEQ2)
ETEQ=ETEQ+ETEQ2)
ETEQ=ETEQ+ETEQ2)
ETEQ=ETEQ+ETEQ2)
ETEQ=ETEQ+ETEQ2)
ETEQ=ETEQ+ETEQ2)
ETEQ=ETEQ+ETEQ2)
ETEQ=ETEQ+ETEQ2)
ETEQ=ETEQ+ETEQ2)
XEQ=XEQ-TEQ/ETEQ
GOTO 51
50 IF (XEQ LT. 0.001) GOTO 2444
T4=T1-273.0
DTQ(C98)-T4
DXEQ(C98)=XEQ
9 CONTINUE
2444 C98=C98-1
CALL ANAL(C98,INCEPT,SLOPE,CORR,DTQ,DXEQ)
AEST=C(X1,INCEPT,SLOPE)
IF(0 .LT. 0) GOTO 802
II=AEST
II=II+9-273
II3=II+9-273
II3=II+9-273
II3=II+9-273
GOTO 201
802 RETURN
END
SUBROUTINE ANAL(C98,INCEPT,SLOPE,CORR,X,Y)
DOUBLE PRECISION AX,AX2,AY,AY2,AXY,INCEPT,CORR,SLOPE,
&X(40),Y(40)
INTEGER LC98,II
II=C98
C98=C98-10
AX=0.00+00
AY=0.00+00
AX2=0.00+00
AY2=0.00+00
254
AXY=0.000

DO 1 I=1,CI8
AX=AX·X(I)
AY=AY·Y(I)
AXX=AXX·X(I)·Y(I)
AY2=AY2·Y(I)·Y(I)
1 CONTINUE
INCEPT=(AXY·AXY·AY2)/(AXX·AY2)
SLOPE=(AY·AY·AY·AY)/((AXX·AY2)·AXX)
CORR=(AY·AY·AY2)/(AY·AY·AY·AY)

DOUBLE PRECISION FUNCTION ENERGY(T,T10,T20)
DOUBLE PRECISION T,T10,T20,F,17
17=1.0·100·1.20
IF (17 LT 300) GOTO 1
IF (17 LT 700) GOTO 2
IF (17 LT 940) GOTO 3
F=8.88909·2.6557·(T-T10)·1.0492·D-3·((T-T10)**2)
F=F+2.7001·D-3·((T-T10)**3)-3.5843·D-9·((T-T10)**4)
GOTO 4
1 F=1.38·T7·1499
GOTO 4
2 F=1.6786·T7·1581
GOTO 4
3 F=1.3099·T7·1331
4 ENERGY=(14.1·T10 + F)**.1.87
RETURN

SUBROUTINE XEQ(T,T,C,XEQ)
DOUBLE PRECISION XXI,T,R,A,A1,AFE,DA1,DA2,DA1FE,J,JI,J,JJ1,JJ2
DOUBLE PRECISION Oil,DEQ,ETEQ,T10,T20,XA,AFEQ,AEQ,ETEQ,TEQ,
JI,J,D1,W1,F,T,TEST,ERROR,T4,XEQ,Fl'RO
I,O,OI,W,W1,F,TEST,ERROR,T4,XEQ,Fl'RO
OI,OS),81,82,1'(7),Y(7),83,AE3T,CC(S)
83=0
C(S)=(000.01)-C(2)-C(3)-C( 4)-C(5)-C(6)-(C7)/C(S)·155.84
C(1)=C(1)/12.011
C(2)=C(2)/28.09
C(3)=C(3)/34.94
C(4)=C(4)/51.71
C(5)=C(5)/5.94
C(6)=C(6)/52.0
C(7)=C(7)/50.94
B1=C(1)+C(2)+C(3)+C(4)+C(5)+C(6)+C(7)+C(8)
DO 107 U=2,7
Y(U)=C(U)/C(7)
107 CONTINUE
DO 106 U=1,7
C(U)=C(U)/C(7)
106 CONTINUE
DO 108 U=2,7
B3=B3+P(U)*Y(U)
B2=B2+Y(U)

108 CONTINUE
IF (B2 .EQ. 0.0) GOTO 455
W=(B3/B2)**0.187
GOTO 456

455 W=8.054.0

456 CONTINUE
X1=C1)
R=4.31432
W1=4.8570.0
H=3.8575.0
S=1.348
201 XEQ=0.1
T=TT
IF (T .LE. 1000) GOTO 20
H1=1.05525
S1=5.34321
GOTO 19
20 H1=1.11198
S1=1.544
19 F=ENERGY(T,T10,T20)
J=1-DEXP(-W/(R*T))
51 DEQ=D5QRT(1-2*(1+2*T)*XEQ+(1+8*T)*XEQ*XEQ)
TEQ=5*DLOG(1-XEQ(1-2*XEQ))
TEQ=TEQ*DLOG(1-2*j+(4*j-1)*XEQ-DEQ(2*j+(2*DEQ-1)))**6
TEQ=TEQ**T-F
IF (DEQ/DEQ <= 1.0) GOTO 50
ETEQ=5*(DEQ+4(1-XEQ)**(1-2*j+(4*j-1)*XEQ-DEQ(2*j+(2*DEQ-1)))**6
ETEQ=ETEQ**R*T
XEQ=XEQ-TEQ/F
GOTO 51
50 RETURN
END

DOUBLE PRECISION FUNCTION ENERGY(T,T10,T20)
DOUBLE PRECISION T,T10,T20,F,T7
T7=T-100*T20
IF (T7 .LT. 300) GOTO 1
IF (T7 .LT. 700) GOTO 2
IF (T7 .LT. 940) GOTO 3
P=8.11890+0.2677*(T7-1140)**2
P=1.3810+0.2677*(T7-1140)**2
P=+2.70103D-2*(T7-1140)**2-3.58434D-2*(T7-1140)**2
GOTO 4
1 F=+1.3810*7.1499
GOTO 4
2 F=+1.65786*7.1581
GOTO 4
3 F=+1.30909*7.1331
4 ENERGY=4.141*T10 + F*4.187
RETURN
END

DOUBLE PRECISION FUNCTION XALPH(T)
DOUBLE PRECISION T,CTEMP
CTEMP=T-273.0D0*0.00305D0*0.002
XALPH=0.1258D-2+0.8816D-2*CTEMP+0.2435D-2*CTEMP=CTEMP*CTEMP
&+0.3417D-2*CTEMP*CTEMP*CTEMP
RETURN
END

256
The motion of austenite/ferrite interface is considered to be parallel to the
inconcentration planes.

The steel is divided into slices of different compositions, \( \Delta t_3 \) temperature
of each slice is calculated and transformation is allowed only in slices
whose \( \Delta t_3 \) temperature is higher than the concerned transformation
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The carbon is not allowed to redistribute among the slices after each
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Typical data set follows:

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<td>0.43 0.60 0.70 0.80 0.90 1.00</td>
<td>0.43 0.60 0.70 0.80 0.90 1.90</td>
</tr>
</tbody>
</table>

\[ \Delta \text{C}(\text{Si, Mn, Ni, Mo, Cr, V)} \]

\[
\text{IMPLICIT REAL }*(\text{A-H,K-Z}), \text{ INTEGER}(L) \\
\text{DOUBLE PRECISION C(10),D(10),XEQ(300)} \\
\Delta \text{C}(\text{Si, Mn, Ni, Mo, Cr, V) = 0} \\
\text{AVEQOL} = \Delta \text{C}(\text{Si, Mn, Ni, Mo, Cr, V)} \\
\text{TVOLF} = 0.000000 \\
\text{ISTOP} = 0 \\
\text{AVEQOL} = 0.000000 \\
\text{TVOLF} = 0.000000 \\
\text{C1} = 0.0 \\
\text{C2} = 0.0 \\
\text{C3} = 0.0 \\
\text{C4} = 0.0 \\
\text{C5} = 0.0 \\
\text{C6} = 0.0 \\
\text{C7} = 0.0 \\
\text{READS} = \text{KELVIN} \\
\text{TISO} = \text{KELVIN} - 273.00 = 0 \\
\text{XALPHA} = \text{xalpha}(\text{KELVIN}) \\
\text{WRITE}(6,9)KELVIN,xALPHA,VINCR \\
\text{WRITE}(6,9,9090) \\
9090 \text{ FORMATT(1)} \\
\text{DO } 1 \text{ I=1,300} \\
\text{READS} = \text{END} = 2(\text{C1}, \text{C2}, \text{C3}, \text{C4}, \text{C5}, \text{C6}, \text{C7}) \\
\text{CN}(0) = \text{C1} \\
\text{NK}(0) = \text{C2} \\
\text{MN}(0) = \text{C3} \\
\text{NY}(0) = \text{C4} \\
\text{MO}(0) = \text{C5} \\
\text{CR}(0) = \text{C6} \\
\text{V}(0) = \text{C7} \\
\text{FE}(0) = 100.00 = 0(\text{C1}+\text{C2}+\text{C3}+\text{C4}+\text{C5}+\text{C6}+\text{C7}) \\
\text{C1} = \text{C1}+\text{C1} \\
\text{C2} = \text{C2}+\text{C2} \\
\text{C3} = \text{C3}+\text{C3} \\
\text{C4} = \text{C4}+\text{C4} \\
\text{C5} = \text{C5}+\text{C5} \\
\text{C6} = \text{C6}+\text{C6} \\
\text{C7} = \text{C7}+\text{C7} \\
\text{DO } 43 \text{ II=1,7} \\
\]
E(U1)&C(U1)

43 CONTINUE
CALL XEQ(KELVIN,XEQ(U1))
CALL TEMP3(TAE3(U1))
XBAR=C(I)
WRITE(6,101)XEQ(U1),TAE3(U1)
WRITE(6,6161)

6161 FORMAT('***********************************************************************

*-----------------------------------------------------------------------*

1 CONTINUE
2 ISLICE=11
WRITE(*,*) ISLICE
I(1)=C1/ISLICE
I(2)=C2/ISLICE
I(3)=C3/ISLICE
I(4)=C4/ISLICE
I(5)=C5/ISLICE
I(6)=C6/ISLICE
DO 10 10=1,1
WD(JU)=I(10)
10 CONTINUE
DO 56 JU=1,1
F(JU)=I(JU)
56 CONTINUE
CALL XEQ(KELVIN,D,XEQH)
CALL TEMP3(F,TAE3H)
WRITE(6,15)TAE3H

15 FORMAT(' TAE3H= ',10.4)
WRITE(*,*) D(I)
D'(TAE3H LT. TISO) OCTO 189
GOTO 85
85 D'(XEQH ll. D(I) GOTO 189
GOT019
19 D'(XEQH .GT. XAIJHA) GOTO 981
GOTO 189
189 VOLH=(XEQH·D(I))/(XEQH.XAIJHA)
GOTO 618
981 VOLH=(XEQH·D(I))
GOTO 981

5329 VOLF(J)=0.00
GOTO 5
5329 VOLF(J)=VOLF(J)+VINCR
XGAMMA(J)=XBAR-((VOLF(J)-XBAR-·XALPHA)/A(1)0.00-VOLF(J))
IF (XGAMMA(J) LE. XEQ(J)) GOTO 4
5 IA(J)=1
ISTOP =ISTOP+IA(J)
VOLF(J)=VOLF(J)+VINCR
IF (VOLF(J) LT. 0.00) GOTO 115
GOTO 4
115 VOLF(J)=0.00
XGAMMA(J)=XBAR
4 CONTINUE
6 CONTINUE
14 DO 12 JJ=1,1ISLICE
AVEVOL=AVEVOL+VOLF(J)
WRITE(6,786U1,VOLF(J),XGAMMA(J),XEQ(J),TAE3(J),XBAR,AVEVOL

786 FORMAT(' SLICE= ',J3,' VOLF= ',01D10.3,' XGAMMA= ',01D10.3,' XEQ= ',
01D10.3,' TAE3= ',01D10.3,' XBAR= ',01D10.3,' AVEVOL= ',RUNNING SUM= ',01D10.3)
12 CONTINUE
WRITEST(13),AVEVOL.

13 FORMAT(' Average volume fraction of transformation', A' in heterogeneous alloy = ',D8.3)
9 FORMAT(' KELVIN = ',F7.0, ' XALPHA, mol. fraction = ',D12.4
, ' VOL. INCREMENT = ',D12.4)
10 FORMAT(' Slice Number = ',I3, ' XEQ = ',D10.4, 
, ' AE3-Ta = ',D10.4)
15 FORMAT(' Maximum volume fraction of bainitic ferrite in ', 
, ' an alloy of average composition = ',D8.3).
STOP

END

C**************************************************************************************************
SUBROUTINE TEMPC(AE3T)
DOUBLE PRECISION X,X1,R,A,A1,AFE,AFE,D1A,D12,D1A1,TAU,HI,S,COREQ,
DOUBLE PRECISION D1I,DTQ(40),DEEQ(40), 
INTEGER T1,T1J,TN0,T8,TAU,TAU1,TAU2,TAU3,TAU4,TAU5,TAU6,TAU7,TAU8,
DOUBLE PRECISION DLI,DTQ(40),DEEQ(40), 
DOEQ,EDEQ,ETEQ,ETEQ2,TEQ,
1J1,J2,J3,J4,J5,J6,J7,J8,J9,J10,J11,J12,J13,J14,J15,J16,J17,J18,J19,J20,
1(CI),B1,B2,P(7),Y(7),B3,AE3T,EE(8)
WRITEST(1100),CI(1),CI(2),CI(3),CI(4),CI(5),CI(6),CI(7)
1100 FORMAT('D11.3)
B=0.0
CI(1)=(100.0-CI(2)-CI(3)-CI(4)-CI(5)-CI(6)-CI(7))/55.84
CI(1)=CI(1)/10.15
CI(2)=CI(2)/28.09
CI(3)=CI(3)/54.94
CI(4)=CI(4)/58.71
CI(5)=CI(5)/95.94
CI(6)=CI(6)/52.0
CI(7)=CI(7)/92.94
B1=C(1)+C(2)+C(3)+C(4)+C(5)+C(6)+C(7)+C(8)
DO 107 U=2,7
Y(U)=C(U)/C(8)
107 CONTINUE
DO 106 U=1,7
C(U)=C(U)/B1
106 CONTINUE
B2=0.0
T1=3*Y(2)+7*Y(3)+5*Y(4)+12*Y(5)+9*Y(6)+7*Y(7)+12
T2=3*Y(2)+7.5*Y(3)+4*Y(4)+26*Y(5)+19*Y(6)+44*Y(7)
T3=3.8464*6*CI(2)**4+2.4232D+07*CI(2)**3+5.6254D+07*CI(2)**2+6.7831D+07*CI(2)+1.0073D+07*CI(2)**2+1.9128D+07*CI(2)+1.0073D+07*CI(2)**2+1.9128D+07*CI(2)+1.0073D+07*CI(2)**2+1.9128D+07*CI(2)+1.0073D+07*CI(2)**2+
T4=3.8464*6*CI(2)**4+2.4232D+07*CI(2)**3+5.6254D+07*CI(2)**2+6.7831D+07*CI(2)+1.0073D+07*CI(2)**2+1.9128D+07*CI(2)+1.0073D+07*CI(2)**2+1.9128D+07*CI(2)+1.0073D+07*CI(2)**2+1.9128D+07*CI(2)+1.0073D+07*CI(2)**2+
T5=3.8464*6*CI(2)**4+2.4232D+07*CI(2)**3+5.6254D+07*CI(2)**2+6.7831D+07*CI(2)+1.0073D+07*CI(2)**2+1.9128D+07*CI(2)+1.0073D+07*CI(2)**2+1.9128D+07*CI(2)+1.0073D+07*CI(2)**2+
T6=3.8464*6*CI(2)**4+2.4232D+07*CI(2)**3+5.6254D+07*CI(2)**2+6.7831D+07*CI(2)+1.0073D+07*CI(2)**2+1.9128D+07*CI(2)+1.0073D+07*CI(2)**2+1.9128D+07*CI(2)+1.0073D+07*CI(2)**2+
DO 108 U=2,7
B3=B3+T2*Y(U)
B2=B2+T1*Y(U)
108 CONTINUE
IF(B2 .EQ. 0.0) GOTO 455
W=(B3/B2)*4.187
GOTO 456
455 W=8Q54.0
456 CONTINUE
XI=CI(1)
R=8.3142
W1=48570.0
H=38575.0
S=13.48
II=473

259
II=173
III=15
II=0

201  XEQ=0.1
INCEPT=1.0D+00
CORR=1.0D+00
SLOPE=1.0D+00
C98=0
C97=0
DO 9 TI=II1,II2,II3
C98=C98+1
T=TI
IF (T LE. 1000) GOTO 20
H1=105525
S1=45.3421
GOTO 19
20  H1=11.1918
$=51.44
19  P=ENERGY(T,T1,T2,T3)
J=1-DEXP-W(T*P)
51  DEQ=DSQRT(T(1-2*(1+T)*XEQ+(1+4*T)*XEQ*XEQ))
TEQ=5*DELOG(T(1-XEQ)*(1-XEQ))
TEQ=TEQ+DEQ*(1-2*(4*T))
TEQ=TEQ(1-2*(4*T))
TEQ=(T(1-XEQ)*(1-2*(4*T)))*DEQ
TEQ=ETEQ*TEQ/ETEQ
XEQ=XEQ+TEQ
GOTO 51
50  IF (XEQ LT. 0.001) GOTO 2444
T4=T1-273.0
DTX=C98=T4
DXE=C98=XEQ
9  CONTINUE
2444  C98=C98-1
CALL ANAL(C98,INCEPT,SLOPE,CORR,DTQ,DXE)
AET=X1- INCEPT-SLOPE
IF (A1 GT. 0) GOTO 802
A1=AET
AII=II+9-273
AII=AII+9-273
AII=1
GOTO 201
802  RETURN
END
SUBROUTINE ANAL(C98,INCEPT,SLOPE,CORR,X,Y)
DOUBLE PRECISION AX,AX2,AY,AY2,AXY,CORR,SLOPE,
& X(40),Y(40)
INTEGER I,C98,I1
II=C98
C98=C98-10
AX=0.0D+00
AY=0.0D+00
AX=0.0D+00
AY=0.0D+00
DO 1 I=1,C98
AX=AX+X(I)
AY=AY+Y(I)
AX=AX+X(I)*Y(I)
AY=AY+X(I)*Y(I)
1 CONTINUE
INCEPT=(AY*AX3-AX*AY)(C98*AX2-AX*AY)
SLOPE=(C98*AY-AX*AY)(C98*AX2-AX*AY)
CORR=(C98*AY-AX*AY)(C98*AY3-AX*AY3)
C98=
RETURN
END
DOUBLE PRECISION FUNCTION ENERGY(T,T10,T20)
DOUBLE PRECISION T,T10,T20,F,n
n=T-loo-T20
IF (11 _LT. 300) GOTO 1
IF (11 LT. 700) GOTO 2
IF (11 LT_ 940) GOTO 3
F_S.88909+0.2657 0(11 -1140)-I.04923D·3 0<(11 -1140)°°2)
F.,J'+2. 700130..6°*<(11-1140)°°3)-3.584340..9°*<(11.1140)°'4)
GOT04
F=1.3Son·1499
GOT04
Z F=1.65786"TI·1581
GOT04
3 F=1.30089"TI-1331
4 ENERGYo(I41-TI0 + F)°4.187
RETURN
END
SUBROllTlNE XEQ3<TT,C,XEQ)
DOUBLE PRECISION XXI,T,R,A,AI,AFE,AIFE,DAI,DA2,DAIFE,H,HI,S,SI
NTEGER ViO,U,B4)99,C99,C9S,C97
DOUBLE PRECISION Dll,
1DEQ,ETEQ,TIO,T20XA,AFEQ,AEQ,ETEQ2, TEQ,
1JJI,D,DI,W,W1,F,TEST ,ERROR,T4,XEQ,FPR0
1,C(S),B I,B2,P(7),Y(7),B3 ,AE3T,CC(S)
B3=O
C(S)=100.0-C( 1)-C(2(2)-C(3)-C(4)-C(5)-C(6)-C(7))/S5.84
C(1)=C(1)/12.0115
C(2)=C(2)/28.09
C(3)=C(3)/54.94
C(4)=C(4)/58.71
C(5)=C(5)/85.94
C(6)=C(6)/52.0
C(7)=C(7)/50.94
B1=C(1)+C(2)+C(3)+C(4)+C(5)+C(6)+C(7)+C(8)
DO 107 U-2,7
107 Continued
DO 106 U-I,7
C(U)=C(U)/B1
DO 106 U-I,7
B2=O.0
T1o=Y(2*4,3)+Y(3)°*Y(4)*Y(5)°*Y(6)*Y(7)*Y(12)-12)
T2o=-Y(2*4,3)-Y(3)+Y(4)*Y(5)°*Y(6)*Y(7)*Y(12)
P2o=2013.9341+763.8167*Cl)+45802.87*C(2)+2-28006.63*C(2)*31
1-3.864D+06*C(2)°°2+2.4233D+07*C(2)°°3+6.9547D+07*C(2)°°6
P3o=2013.9341+763.8167*C(3)+628.72*C(3)°°2+2.2167.96*C(3)°°3-
12.0119D+06*C(3)°°4+3.1916D+07*C(3)°°5+5.3859D+08*C(3)°°6
P4o=2006.8071+2350.3463*45915.32*C(4)+61600+60*C(4)*3
1-2.4968D+07*C(4)*4+1.8883D+08*C(4)*5+5.5551D+08*C(4)*6
P5o=2006.834-2997.314*C(5)+37906.61*C(5)+21.0328D+06*C(5)*3
1-1.336D+07*C(5)*4+4.8.411D+07*C(5)°°5+5.2.0826D+08*C(5)*6
P6o=2012.567-9224.2655*C(6)+33657.8*C(6)+2-56827.83*C(6)*3
1+8.578D+06*C(6)*4-8.7482D+07*C(6)*5+2.0839D+08*C(6)*6
P7o=2011.9996+6347.9118*C(7)+541.7566*C(7)*2
1-2501.81085*C(7)*3-4.1676D+06*C(7)*4
DO 108 U=2,7
B3=B3+P(U)*Y(U)
B2=B2+Y(U)
108 Continued
IF(B2.EQ. 0.0) GOTO 455
W=(B3/B2)°4.187
GOTO 456
CONTINUE
X1=Q1()
R=3.31432
W1=48570.0
H=38575.0
S=13.48
201 XEQ=0.1
T=TT
IF (T .LT. 1000) GOTO 20
H1=405525
S1=43.3521
GOTO 19
20
H1=111918
S1=51.44
19 F=ENERGY(T,T10,T20)
J=1-DEXP(W/(X1))
51 DEQ=DSQRT((1-2*E)*XEQ+1*(1+8*E)*XEQ*TEQ)
TEQ=TEQ+4LOG((1-2*E)*XEQ+(1+8*E)*XEQ-DEQ)*((1-2*E)*XEQ-DEQ)
TEQ=2*TEQ+F
IF (DABS(TEQ) .LT. 1.0) GOTO 51
ETE=O.E-(I-T10)/(T-T20)
ETE=ETE+ETE2+F
ETE=(ETE+ETE2)*/F
XEQ=XEQ-TEQ/ETE
GOTO 51
50 RETURN
END
DOUBLPRECISION FUNCTION ENERGY(T,T10,T20)
DOUBLPRECISION T,T10,T20,F,F7
T7=T-1000*T20
IF (T7 .LT. 300) GOTO 1
IF (T7 .LT. 700) GOTO 2
IF (T7 .LT. 940) GOTO 3
F=8.38909+0.26557*(T7-1140)-1.04923*(T7-1140)**2
GOTO 4
F=F+2.70013*6*(T7-1140)**3-3.8434*9*(T7-1140)**4
GOTO 4
2 F=1.65786*T7-1581
GOTO 4
3 F=1.30089*T7-1331
4 ENERGY=O.41*T10+F)*4.187
RETURN
END
DOUBLPRECISION FUNCTION XALPH(T)
DOUBLPRECISION T,CTEMP
CTEMP=T/273.0D+00/900.0D+00
XALPH=O.135RD-02-0.9816D-02*CTEMP+0.3650D-01*CTEMP*CTEMP
&+0.8170D-01*CTEMP*CTEMP*CTEMP
RETURN
END
APPENDIX-5

C Copyright S. A. Khan, H. K. D. H. Bhadechia.
C
C Program calculates volume fraction of martensite from dilatometric data.
C
C Typical dataset follows
C VBAIN=r% C in residual aust.-Ms
C 0.142 0.508 262.0
C relative length change-respective temp
C 0.0057 100.00
C 0.0053 120.00
C VBAIN calculated from dilatometry using prog length
C r% C in residual aust from dilatometry using prog length
C Ms from cooling curve from dilatometry
C Relative length change & respective temp obtained from cooling curve
C A1, C1, GI are the martensite a, martensite c and austenite lattice parameters
C See Andrews and Speich for details of parameters as a function of alloy
C For lattice parameter equations, substitutional alloy content in atomic %
C but carbon in wt. %
C VBAIN = bainite volume fraction;
C MS = martensite start temperature XWT = carbon content of residual austenite
C T = Centigrade (all temps in these units) L = relative length change
C
IMPLICIT REAL*8 (A-H,L-Z), INTEGER (I-K)
DOUBLE PRECISION X(SOO),Y(SOO),RESULT(200)
READ(S,·) VBAIN,xwT,MS
VBAIN=V0+0.5*VBAIN
WRITE(6,9)VBAIN ,xwT,MS
WRITE(6,6)EXA,EXY
MS=0.66
SL=3.55
VAN=0.1
CR=0.86
N=1.70
MO=0.22
WRITE(6,7) XWT,SL,MN,N,M0,CR,VAN
ALLOY1=0.001*MN+0.0002*SI+0.0001*Cr+0.0053*Mo+0.0017*VAN
ALLOY2=0.0006*MN+0.0009*N0+0.0006*Cr-0.0003*SI
G1=3.575+ALLOY1+0.033*XWT
A1=2.661+ALLOY2-0.013*XWT
C1=2.661+ALLOY2+0.116*XWT
WRITE(6,5)
DO 1 K=1,500
READ5,*END=23,T
C Calculation of lattice parameters at temperature T
G2=G1*(1.0D+0+(T-20.0)*EXY)
A2=A1*(1.0D+0+(T-20.0)*EXA)
C2=C1*(1.0D+0+(T-20.0)*EXA)
C Calculation of the volume fraction of martensite
V2=(A2*L2*G2**3)*(V0**4*(A2**2*A2**2-C2**2-G2**2**3))
C V2 is the fraction of residual austenite that transforms into martensite
C V2 = f = VM/Vg
C Calculation of In(1-f)
IF (V2 .GT. 1) GOTO 22
GOTO 23
22 V2=0.999
23 Y(K)=D0.00X(1.0D+0-(V2))
X(K)=MS-T
YGR=V0*(Y2**VG)
C TO read every 3rd data from the computed (dilatometric) length change data.
NO=NO+1
IF (NO .EQ. 3) GOTO 67
GOTO 71
C Not to consider data below 15.0 degree centigrade.
67 IF (T.LT. 15.0) GOTO 68
GOTO 71

263
C Calculating the absolute volume fraction
IF (T LE. 20.0) GO TO 123
GO TO 321
123 VALPV2'VGR
WRITE(6,66) T, VAB
66 FORMAT (* ABSOLUTE VALUE OF MARTENSITE AT 'F4.0', 'S=' 'F8.3)
321 NO=0
II=II+1
3 FORMAT (F8.5,F3.0,F7.3,F10.5,F10.5,F7.0,F10.3,F10.4)
1 CONTINUE
2 III=K-1
STOP
4 FORMAT(* Volume Fraction of Bainite = ', F8.4/
& ' C in residual austenite, at ', 
& ' time of bainite reaction, wt.% = ', F8.3/
& ' Martensite start temperature, centigrade = ', F8.2)
7 FORMAT(* C, wt.% = ',F8.2X,'Si, wt.% = ',
& 'Cr, wt.% = ',F8.2X,'Mo, wt.% = ',F8.2,
& 'P, wt.% = ',F8.2X,'Al, wt.% = ',F8.2,
& ', wt.% = ',F8.2X,'Mn, wt.% = ',F8.2,
& 'N, wt.% = ',F8.2X,'Cu, wt.% = ',F8.2,
& 'V, wt.% = ',F8.2X,'Ni, wt.% = ',F8.2,
& 'Co, wt.% = ',F8.2X,'Mo, wt.% = ',F8.2)
6 FORMAT(* Linear Expansivity, alpha = ',D12.4/
& ' Linear Expansivity, gamma = ',D12.4)
5 FORMAT(* Length Comp Vmart G2 A2 C2 ',
& ', ',
& ' Ms-Tq LN(1-F) VGR')
END
C The steel is divided into slices of different compositions,
C Aec temperature and XEQ of the first slice (before depleted) is calculated.
C Transformation is allowed to go to 100% in slice J=1 if its Aec temperature
C is higher than the isothermal temperature, the carbon thus
C ejected is allowed to homogenize in the residual austenite.
C Transformation now shifts to slice J=2 if its Aec temperature, calculated
C from its new composition (i.e., due to increase in carbon content), is
C higher than the concerned transformation temperature. The excess of
C transformation is limited by paraequilibrium mechanism.
C The results are averaged and compared with a steel of the corresponding average
C composition.

C Typical dataset follows:
C 673 (temperature in Kelvin)
C 0.43 0.50 0.60 0.70 0.80 0.90 1.00 (Composition of slice 1 in wt. %)
C 0.43 0.60 0.70 0.80 0.90 1.00 (Composition of slice 2 in wt. %)
C C Si Mn Ni Mo Cr V

C IMPLICIT REAL*8(A-H,K-Z), INTEGER(I)
C DOUBLE PRECISION C(S),D(8),XEQ(200)
C E(8),F(8),V(200)
C &E(8),V(200),W(8),CD(200),G(200),TAE3(200)
C TAE3X(200),TVOLF,AVEVOL,MOMENT,TISO,SLICE,TSLICE
C DIMENSION VOLFD(200)
C VINC=0.000002D+00
C SCR=0.0
C AVEVOL=0.0D+00
C TVOLF=0.0D+00
C 
C READ(S,')KEL VIN
C TISO=KEL VIN-273.0D+0
C XAUXA-XAUXH(KEL V IN)
C WRITE(6,4444)
C 4444 FOR..'
C WRITE(6,9090)
C 9090 fOR.
C DO 1 I=1,200
C READ(S,' )l,'IDs2)C(1),C(2),C(3),C(4),C(5),C(6),C(7)
C C1=C1
C C2=C2
C C3=C3
C C4=C4
C C5=C5
C C6=C6
C C7=C7
C READ(X5,*)KEL VIN
C TISO=XEL VIN-273.0D+0
C XALPHA=XALPHA(KEL VIN)
C WRITE(8,4444)
C 4444 FORMAT(****CARBON IS ALLOWED TO DIFFUSE!!!!!!!!!!!')
C WRITE(8,9090)KEL VIN,XALPHA,VINC
C WRITE(8,9090)KEL VIN,XALPHA,VINC
C WRITE(8,9090)KEL VIN,XALPHA,VINC
C
C6=C6+C(6)
C7~+C(7)
DO 43 U1=1,7
E(U1)=C(U1)
43 CONTINUE
CALL XEQ(KELVIN,CD(XEQ(I))
CALL TEMPX,TAE(X)
XBAR=C(I)
WRITE(6,10)XEQ(0,TAE(I))
WRITE(6,10)
10 FORMAT(************

1 CONTINUE
2 ISLICE=I-1
WRITE(10,1)ISLICE
D(1)=C(1)/ISLICE
D(2)=C(2)/ISLICE
D(3)=C(3)/ISLICE
D(4)=C(4)/ISLICE
D(5)=C(5)/ISLICE
D(6)=C(6)/ISLICE
D(7)=C(7)/ISLICE
DO 70 J1=1,7
D(J1)=D(J1)
70 CONTINUE
DO 56 J1=1,7
F(J1)=D(J1)
56 CONTINUE
CALL XEQ(KELVIN,C,xEQ(I»
CALL TDIP3(E,T AE(J))
XBAR=C(I)
WRITE(6,10)I,XEQ(I),TABm
WRITE(6,6161)
6161 FOR...

1 COl'ITU',lJE
2 SLICE=I-1
WRITE(10,1) SLICE
TSLICE=
IF (XEQ(J) .LE. AVEX) GOTO 5
GOTO 7007
7007 IF (TAB(J) LT. TISO) GOTO 5
GOTO 9352
9352 AVEVOL=SLICE/TSLICE
VOLF(J)=AVEVOL
AVEX=D(J)+AVEVOL*(D(J)+XALPHA)/(1.00+0.00-AVEVOL)
WRITE(6,886)SLICE,J, XEQ(J),XALPHA,AVEVOL,AVEX,VOLF(J)
886 FORMAT(' SLICE=',J,' ',XEQ(J),' ',XALPHA=',

C Recalling the original composition (wt%) for each slice......
C(D(1)=CN(J+1)
C(D(2)=SI(J+1)
C(D(3)=MN(J+1)
C(D(4)=Nl(J+1)
C(D(5)=MO(J+1)
C(D(6)=CR(J+1)
C(D(7)=V(J+1)
XG(J+J)=CD(1)+XG(J+J)*CD(1)/(1.00+0.00-VOLF(J))

C Getting new composition (wt%) of residual assemblage in each slice
RT=(100.00+0.00-XG(J+J))*100.00+0.00-CD(1))
CD(I)=XG(J+I)
DO 262 N0=1,7
CD(N0)=CD(N0)
262 CONTINUE
DO 161 NO=1,7
CEOlO)(D(NO)
161 CONTINUE
CALL XI(QXKELVIN,CD,XEQ(J+I))
CALL TEMP3(C,TAEXI+I))
GOTO 4
4 CONTINUE
GOTO 786
786 WRITE(6,113)AVEVOL
13 FORMAT' Average volume fraction of transformation',
&' in heterogeneous alloy =',D9.3)
9 FORMAT' KELVIN = ',F7.0,' XALPHA, mol. fraction =',D12.4
&', VOLT\ INCREMENT=',D12.4)
10 FORMAT' Elion Numbers 'J3,'
&' XEQ = ',D10.4,',
&' AE3=Te ',D10.4)
15 FORMAT' Maximum volume fraction of bainitic ferrite in ',
&' an alloy of average composition =',D9.3)
STOP
END

C*******************************************************************************************************
SUBROUTINE TEMP3(C,AE3)
DOUBLE PRECISION XXI,RA,AA1,APF,ALPHA1,DA1,DA2,DA1FEJ,UE,1,5,51
INTEGER TL,N0,U,669,99,98,99,97
DOUBLE PRECISION D1,D1O,DSEQ(40),
1INCEP,SLQ,COER,
1DEQ,ETEQ,110,11C,DDAO,APF,AE,SEQ,ETEQ2,TEQ,
1J1,J2,J3,J4,1J5,1J6,1J7,TEQ,0,1J9,QQK0
11,12,17,18,199,C99,C95,C97
DOUBLE PRECISION D11,DTQ(40),DXEQ(40),
1INCEP,SLQ,COER,
1DEQ,ETEQ,110,11C,DDAO,APF,AE,SEQ,ETEQ2,TEQ,
1J1,J2,J3,J4,1J5,1J6,1J7,TEQ,0,1J9,QQK0
11,12,17,18,199,C99,C95,C97
1100 FORMAT(D11,3)
B3=0
C(9)=(100.0-C(1)-C(2)-C(3)-C(4)-C(5)-C(6)-C(7))55.84
C(11)=C(1)/12.0115
C(2)=C(2)/28.09
C(3)=C(3)/54.94
C(4)=C(4)/71
C(5)=C(5)/5.94
C(6)=C(6)/52.0
C(7)=C(7)/50.34
B1=1(C1+C2+C3+C4+C5+C6+C7+C8)
DO 107 U=2,7
Y(U)=C(U)/C(B1)
107 CONTINUE
DO 106 U=1,7
C(U)>C(U)/B1
106 CONTINUE

B3=0.0
T1=1(Y(2)*Y(3)+Y(3)**2+Y(4)**2+Y(5)**2+Y(6)**2+Y(7)**2+Y(8)**2+Y(9)**2+Y(10)**2+Y(11)**2+Y(12)**2)
T2=3(Y(2)**2+Y(3)**2+Y(4)**2+Y(5)**2+Y(6)**2+Y(7)**2+Y(8)**2+Y(9)**2+Y(10)**2+Y(11)**2+Y(12)**2+Y(13)**2)
1=3.864D+06*C(2)**4*2.4233D+07*C(2)**5+6.9547D+07*C(2)**6
P(2)=201.3241+76.8167*C(2)+4560.87*C(2)**2*28001.63*C(2)**3
P(3)=201.3241+76.8167*C(2)+4560.87*C(2)**2*28001.63*C(2)**3
12.DO110D+06*C(3)**4+3.1716D+07*C(3)**5+5.1383D+08*C(3)**6
P(4)=2006.8017+2300.2424*C(4)-54915.32*C(4)**2+1.0232D+06*C(4)**3
1-2.4968D+07*C(4)**4+1.8838D+08*C(4)**5+5.5531D+08*C(4)**6
P(5)=2006.8017+2300.2424*C(5)-54915.32*C(5)**2+1.0232D+06*C(5)**3
1-1.3308D+07*C(4)**4+4.8141D+07*C(5)**5+2.0383D+07*C(5)**6
P(6)=2012.367+9224.265*C(6)-35657.87*C(6)**2+2.5668D+08*C(6)**3
1-8.5676D+06*C(6)**4+6.6748D+07*C(6)**5+2.0837D+08*C(6)**6
P(7)=211.9996+5247.9118*C(7)+541.7566*C(7)**2
1+250.11.81057*C(7)**3+3.4-16786D+06*C(7)**4
DO 108 U=2,7
B3=B3+P(U)**Y(U)
108 B3=B3+Y(U)
CONTINUE
BYR=1.EQ.0.0) GOTO 455
W=(13/362)*4.287
GOTO 456
455 W=8054.0
456 CONTINUE
X1=C(1)
R=8.31432
W=448570.0
H=347575.0
S=11.48
II=873
II=1173
II=15
II=0
201 XEQ=0.1
INCEPT=1.0D+00
CORR=1.0D+00
SLOPE=1.2D+00
C98=0
C97=0
DO 9 T1=III,III,1D
C98=C98+1
T=T1
IF (T .LE. 1000) GOTO 20
H1=105525
S1=5.34512
GOTO 19
20 H1=111918
S1=51.44
9 F=EENERGY(T,T10,T20)
T1=DEXP(-W/(R*T1))
51 DEQ=DQRT(1-2*12(1+2*12)*XEQ(1+2*12)*XEQ)XEQ)
TEQ=T*QRT(1-XEQ(1-2*12))
TEQ=TEQ+DLOG((1-2*12)*(1+2*12))
TEQ=TEQ*R*T
IF (TABS(TEQ).LT.1.0) GOTO 50
ETEQ=6*S*EENERGY(T10,T20)+6*EENERGY(T10,T20)+6*EENERGY(T10,T20)
ETEQ=ETEQ*ETEQ+ETEQ/"R"T
XEQ=XEQ-TEQ/ETEQ
GOTO 51
50 IF (XEQ .LT. 0.001) GOTO 2444
T4=T1-273.0
DTQ(C98)=T4
DXEQ(C98)=XEQ
9 CONTINUE
2444 C98=C98-1
CALL ANAL(C98,INCEPT,SLOPE,CORR,DTQ,DXEQ)
AET=(C1-INCEPT)/SLOPE
BFI (1.0) GOTO 822
I=AET
II=II+9.273
II=II+9.273
II=II+9.273
GOTO 201
822 RETURN
END
SUBROUTINE ANAL(C98,INCEPT,SLOPE,CORR,X,Y)
DOUBLE PRECISION AX,AX2,AY,A,AY2,INCEPT,CORR,SLOPE,
&X(40),Y(40)
INTEGER C98,J1
I=1298
C98=C98-10
AX=0.0D+00
AY=0.0D+00
AX2=0.0D+00
AY2=0.0D+00
AXY=0.00+0.0
DO I=1,NS
AX=AX+X(I)
AY=AY+Y(I)
AXY=AXY+X(I)*Y(I)
AX2=AX2+X(I)*X(I)
AY2=AY2+Y(I)*Y(I)
1 CONTINUE
INCEPT=(AXY*X2+AX-X2+AX)*CS
SLOPE=(AXY-X2+AX)*DSQRT((AXY+AX-X2+AX)*CS)
CR=R=(CS*AXY-CS*AY)/((CS+AX2-CS*AX))
C98=11
RETURN
END

DOUBLE PRECISION FUNCTION ENERGY(T10,T20)
DOUBLE PRECISION T,T10,T20,F,T7
T7=T-100*T20
IF (T7 .LT. 300) GOTO 1
IF (T7 .LT. 700) GOTO 2
IF (T7 .LT. 940) GOTO 3
F=-8.88909+0.26577 -(T7 -1140)-1.049230-3 *(T7 -1140)' '2
F=F+2.700130-6'«(11-1140)-3)-3.584340-9*(T7-1140)**2
GOTO 4
F=1.35*T7-1499
GOTO 4
2 F=1.65786*T7-1581
GOTO 4
3 F=1.30897*T7-1331
4 ENERGY=(141*T10 + F)*4.187
RETURN
END

C********************************************************************
SUBROUTINE XEQ3(IT,C,XEQ)
DOUBLE PRECISION XXI,T ,R.A,AI ,AFII ,AlFE,DAl,DA2,DAlFE,H,HI,S,SI,
INTEGER I,NO,U,II4)99,C99,C9S,C97
DOUBLE PRECISION OIl,
10EQ,ETEQ,T10,T20,XA,AFEQ,AEQ ,ETEQ2, TEQ,
IJ)I,D,DI,W,WI .F,TEST ,ERROR, T4,XEQ,FPRO,
I<(S),B I ,B2,P(7), Y(7),B3 .AE3T,CC(S)
83=0
C(S)-(I oo.().<( 1)-C(2)-C(3)-C(4 )-C(5)-<:( 6)-(C7))/55.84
C(1)=C(1)/12.0115
C(2)ooC(2)/28.09
C(3)ooC(3)/54.94
C(4)=C(4)/95.94
C(5)=C(5)/55.0
C(6)=C(6)/50.0
C(7)=C(7)/50.94
B1=C(1)+C(2)+C(3)+C(4)+C(5)+C(6)+C(7)+C(8)
DO 107 U=2,7
Y(U)=C(U)/C(8)
107 CONTINUE
DO 106 U=2,7
C(U)=C(U)/C(8)
106 CONTINUE
82=0.0
n
Y(2)*( -3)+ Y(3)*2+ Y(4)'12+ Y(5)*( -9)+ Y(6)'(·I)+ Y(7)'( -12)
~3'
Y(2)-37.5
""""Y(3)-6"Y(4)- 26"Y(5)-19 'Y(6)-44 'Y(7)
1+3.8640+06"C(2)11"4-2.42330+07'C(2)12+6.95470+07*C(2)13
1+3.8640+06"C(2)11"4-2.42330+07'C(2)12+6.95470+07*C(2)13
1+3.8640+06"C(2)11"4-2.42330+07'C(2)12+6.95470+07*C(2)13
1-2.49680+07 *C(2)+1.83380+06*C(2)+5.555310+06*C(2)+2.1647.96*C(2)
1-2.49680+07 *C(2)+1.83380+06*C(2)+5.555310+06*C(2)+2.1647.96*C(2)
1-2.49680+07 *C(2)+1.83380+06*C(2)+5.555310+06*C(2)+2.1647.96*C(2)
1-2.49680+07 *C(2)+1.83380+06*C(2)+5.555310+06*C(2)+2.1647.96*C(2)

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1·1.3306D+07·C(5)**4+8.411D+07·C(5)**5+2.0826D+08·C(5)**6
P(6)=201.2367-924.2665·C(6)+3365.8·C(6)**2+2.5682783·C(6)**3
1+8.567D+06·C(6)**4+6.7482D+07·C(6)**5+2.0837D+08·C(6)**6
P(7)=2011.9999-6247.9118·C(7)+5411.7566·C(7)**2
1+2501.18·1085·C(7)**3+4.1676D+07·C(7)**4
DO 108 U=2,7
B3=B3+Y(U)
B3=B3+Y(U)
108 CONTINUE

IF(B2.EQ.0.0) GOTO 455
W=W(B2)**4.187
GOTO 456

455 W=8054.0

456 CONTINUE

X1=CT(1)
R=6.31432
W1=46570.0
H=48575.0
S=13.48

201 XEQ=0.11
T=TT
IF (T.LT.1000) GOTO 20
H1=10535
S1=45.34521
GOTO 19

20 H1=111918
S1=51.44

19 F=ENERGY(T,T10,T20)
J=1-DEXP-W(R*T)
51 DEQ=D(SQRT(1-(1.2+1.7)**XEQ)+(1.8+1.8)*XEQ*XEQ))
TEQ=5.0LOG(1-XEQ(1-2*XEQ))
TEQ=TEQ-TEQ**9**T
IF (JATOMIC) LT. 1.0) GOTO 50
ETEQ=5.0LOG(1-XEQ(1+2*XEQ))
ETEQ=ETEQ+ETEQ**9**T
XEQ=XEQ-ETEQ
GOTO 51
50 RETURN
END

DOUBU> PRECISION FUNCTION I!NERGY(T,T10,T20)
DOUBU> PRECISION T,T10,T20,P,T7
T7,T-1000'T20
IF (T7 .LT. 300) GOTO 1
IF (T7 .LT. 700) GOTO 2
IF (T7 .LT. 940) GOTO 3
F=8.118909+0.2657*(T7·1040)-1.04923D-3*(T7·1040)**2
P=8.88996+0.2657*(T7·1040)-1.04923D-3*(T7·1040)**2
GOTO 4

1 F=1.38*T7-1499
GOTO 4

2 F=1.65786*T7-1581
GOTO 4

3 F=1.30089*T7-1331

4 ENERGY=J*(T10 + F)**4.187
RETURN
END

DOUBU> PRECISION FUNCTION XALPH(T)
DOUBU> PRECISION T,CTEMP
CTEMP=CT·273.0D+00+900.0D+00
XALPH=0.13260·0.8818D-02·CTEMP·0.345D-01·CTEMP·CTEMP
&+0.24170·0·CTEMP·CTEMP·CTEMP
&+0.69662D-02·CTEMP·CTEMP·CTEMP·CTEMP
RETURN
END