THE ROLE OF INTERFACE MOBILITY ON THE KINETICS OF DIFFUSIONAL TRANSFORMATION IN FE-C AND FE-MN ALLOYS

G.P. Krielaart and S. van der Zwaag
Laboratory for Materials Science, Delft University of Technology,
Rotterdamseweg 137, 2628 AL Delft, the Netherlands.

ABSTRACT
Models to describe the kinetics of growth of (pro-eutectoid) ferrite during the transformation \( \gamma \rightarrow \alpha \) in Fe-C and low Mn Fe-Mn alloys are discussed. The transformation in the Fe-Mn alloys is modelled using an interface controlled growth model. It is assumed that the interface mobility is proportional to the chemical potential difference of the Fe-lattice. The interface mobility has a simple exponential temperature dependence. In Fe-C alloys, mixed control of growth is established by taking into account the effects of both the intrinsic interface mobility and carbon volume diffusion on the conditions prevailing at the interface. The mode of control is predicted to vary from essentially a diffusion controlled mode at very low undercooling towards essentially an interface controlled mode at deep undercoolings. The results from this model are in good agreement with measured growth distances and the corresponding carbon concentration profiles of partially transformed Fe-C alloys.

Introduction
The simplest model systems for plain-carbon steels are binary Fe-C alloys. Despite numerous studies (see e.g. Enomoto, 1992; Crusius et al., 1992), the nature and the kinetics of the austenite decomposition even in this simple system are not yet fully understood. Two situations can be distinguished. At transformation temperatures above 1000 K the decomposition of austenite leads to the formation of (pro-eutectoid) ferrite and austenite enriched in carbon. At transformation temperatures below 1000 K a two-step process occurs: the austenite decomposes into pro-eutectoid ferrite and enriched austenite. The enriched austenite subsequently decomposes into a layered structure of ferrite and cementite (Fe3C), called pearlite, once the maximum solubility is reached.

The ratio of the (pro-eutectoid) ferrite to pearlite volume fractions is not a constant but depends on the transformation temperature.

The growth kinetics of the austenite/ferrite transformation is usually modelled assuming local equilibrium at the moving \( \alpha/\gamma \) interface. The C concentration in the austenite at the interface is equal to the concentration indicated by the \((\gamma+\alpha)/\gamma\) phase boundary in the Fe-C phase diagram, irrespective of the degree of the transformation. The transformation proceeds as a consequence of long range carbon diffusion into the remaining austenite grain. This model works well for transformation temperatures above the \( A_1 \) temperature. However, these models
are less successful in predicting the transformation behaviour below \( A_1 \), in particular in predicting the transition from pro-eutectoid ferrite formation to the onset of pearlite formation. In diffusional growth kinetics it is assumed that the growth kinetics is only determined by long range diffusion of the carbon atoms and that interfacial reactions are of no importance for the growth kinetics. However, very little quantitative information about the intrinsic \( \alpha/\gamma \) interface mobility itself is available (Wilson, 1994, 1991; Ågren, 1989; Salwén, 1993; Hillert, 1975). The effect of the interface mobility on the growth kinetics can be determined by examining the kinetics of the transformation \( \gamma \rightarrow \alpha \) in Fe-Mn alloys with low Mn content, i.e. by excluding the effects of carbon. As the mobility of Mn is Fe is very low (e.g. Landholt-Börnstein, 1990), it is possible to cool the Fe-Mn alloy from the \( \gamma \) one-phase region through the \( \alpha/\gamma \) two-phase region into the \( \alpha \) one-phase region without significant diffusional growth and Mn redistribution in the \( \alpha/\gamma \) two-phase region. Transformation of the alloys used, occurs almost entirely in the \( \alpha \) one-phase region and is therefore composition invariant. The growth velocity of these ferrite particles is entirely controlled by the mobility of the \( \alpha/\gamma \) interface.

The analysis of diffusional growth by mixed control, discussed in this work, has essentially the same starting point as the usual analysis of diffusion controlled growth. It starts by assembling the mass balance for carbon rearrangement at the interface. However, the interface velocity is principally determined by the intrinsic \( \alpha/\gamma \) interface mobility (Krielaart and van der Zwaag, 1995a). The interface mobility is therefore incorporated explicitly in the mass balance. The interface velocity determines the carbon mass flux through the interface. The simultaneous carbon redistribution ahead of the advancing interface affects the driving force for interface migration. A major advantage of such a treatment is that principally no prior assumption about the carbon concentration at the interface is required. The carbon concentrations at the \( \alpha/\gamma \)-interface may vary with time. Clearly, in this case, the diffusional growth of ferrite from supersaturated austenite proceeds by non-equilibrium interface conditions. For reasons of simplicity, one-dimensional growth of a flat interface is considered only.

**Interface Mobility**

The relative simplicity of the transformation phenomena in low Mn Fe-Mn alloys permits the use of a fairly simple kinetic model mobility (Krielaart and van der Zwaag, 1995a). It will be discussed briefly here. If the \( \alpha/\gamma \)-interface is essentially disordered, the movement of the interface can be considered to be caused by a diffusion-like transfer of atoms across the interface. The distances of displacement are short and, effectively, it is the interface that moves. For such an interface, it can be argued that there is a linear relationship between the interface velocity and the driving force (not considering the temperature dependence of the factor of proportionality). The key assumption of the model is that the interface velocity \( v \) is equal to the product of the interface mobility \( M \) and the difference of the chemical potential of iron \( \Delta \mu_{Fe} \) on either side of the interface:

\[
v = M \cdot \Delta \mu_{Fe}.
\]

(1)

The interface mobility is assumed to have a simple exponential temperature dependence:

\[
M = M_0 \exp\left(-\frac{E}{RT}\right).
\]

(2)
where $E$ is the energy of activation for interface migration and $M_0$ a pre-exponential factor. The chemical potential difference of iron in the ferritic and in the austenitic state is defined as:

$$\Delta \mu_{Fe} = \mu_{Fe}^\gamma (x_{Mn}^\gamma) - \mu_{Fe}^\alpha (x_{Mn}^\alpha).$$  \hfill (3)$$

and is calculated using the regular solid solution model for Fe-Mn alloys following Kirchner et al. (1973).

To calculate the macroscopic transformation rates during the $\gamma \rightarrow \alpha$ transformation (i.e. the fraction transformed as a function of time and temperature), additional assumptions have to be made concerning the ferrite nucleation; uniformly along the original austenite grain boundary and no nucleation until a temperature below the $A_1$ temperature is reached. The austenite grains are assumed to have a spherical geometry. The ferrite fraction $X^\alpha$ of a single austenite grain then follows from:

$$X^\alpha = \begin{cases} 
1 - \left(\frac{2a}{d_\gamma}\right) & (2a < d_\gamma) \\
1 & (2a > d_\gamma)
\end{cases}$$

where $a$ is the position of the $\alpha/\gamma$-interface and $d_\gamma$ is the diameter of the former austenite grain. The value of $a$ is determined using Eq. (1). The link with the overall transformation kinetics is established by assuming the presence of a log-normal distribution of the austenite grain size from which the average ferrite fraction can be computed.

Experimentally, the ferrite fractions transformed are determined from the heat-effects during the transformation $\gamma \rightarrow \alpha$ in Fe-1mass%Mn and Fe-2mass%Mn alloys using Differential Scanning Calorimetry (DSC). The measured heat capacities, corrected for instrumental effects, during continuous cooling from the $\gamma$ one-phase region are shown in Fig. 1 (Krielaart et al., 1994a).

To check for the reliability of the results, each sample has been used twice, using intermediate annealing at 1173 K. The difference during the transformation is due to the change in the austenite grain size, which affects the transformation kinetics. The heat capacity curves of the Fe-1%Mn alloy exhibit two peaks. The high temperature peak is due to the transformation itself and the low temperature peak is due to the ferromagnetic transformation. The heat capacities curves for the Fe-2%Mn alloy only show one peak, containing both the heat of transformation and the ferromagnetic contribution to the heat capacity of ferrite.

The fractions transformed are extracted from the measured heat-capacity $C_P$ by considering that $C_P$ is a weighed average of the heat-capacities of austenite, ferrite as well as the heat of transformation 1 (Krielaart et al., 1994a):

$$\frac{dx\gamma}{dT} = \frac{C_P^\alpha - C_P^\gamma}{\Delta H^\alpha/\gamma} \cdot x\gamma - \frac{C_P^\alpha - C_P}{\Delta H^\alpha/\gamma},$$

where $C_P^\alpha$ and $C_P^\gamma$ are the heat capacities of ferrite and austenite respectively and $x\gamma$ is the ferrite fraction. the enthalpy difference between austenite and ferrite $\Delta H^{\alpha/\gamma}$ can be determined from the measurements using the relation:
The first evidence for a sluggish interfacial reaction is obtained from the total heat of transformation. According to Table 1, the total amount of heat of transformation tends to increase with increasing cooling rate. This is a consequence of a finite transformation rate in conjunction with the increasing of $\Delta H^{\alpha/\alpha}$ with decreasing temperature. This effect is most clearly visible in the results for the Fe-2\%Mn alloys, where the phase transformation occurs in the vicinity of the Curie temperature of ferrite. The ferromagnetic transition has a fairly strong effect on the enthalpy difference between austenite and ferrite and hence on the total heat of transformation. For the Fe-2\%Mn alloys, the total heat of transformation at a cooling rate of 5 K/min is relatively small as compared to the higher cooling rates. The transformation process at this cooling rate takes place mainly at temperatures well above $T_C$ for the Fe-2\%Mn alloy, which explains the difference. Note that the total heat of transformation tends to decrease with the increasing of the Mn-concentration.
Table 1: The total amount of heat of transformation $Q$ released by the sample resulting from the transformation $\gamma \rightarrow \alpha$ for the Fe-2%Mn alloy at the various cooling rates used. The experimental accuracy is approximately 0.03 kJ/mole.

<table>
<thead>
<tr>
<th>Cooling rate (K/min)</th>
<th>$Q$ (kJ/mole) Fe1%Mn Scan 1</th>
<th>$Q$ (kJ/mole) Fe1%Mn Scan 2</th>
<th>$Q$ (kJ/mole) Fe2%Mn Scan 1</th>
<th>$Q$ (kJ/mole) Fe2%Mn Scan 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>1.10</td>
<td>1.08</td>
<td>1.16</td>
<td>1.20</td>
</tr>
<tr>
<td>10</td>
<td>1.17</td>
<td>1.12</td>
<td>1.59</td>
<td>1.48</td>
</tr>
<tr>
<td>20</td>
<td>1.21</td>
<td>1.16</td>
<td>1.70</td>
<td>1.65</td>
</tr>
</tbody>
</table>

Figure 2: Austenite fractions as a function of temperature during the transformation $\gamma \rightarrow \alpha$ in the Fe-1%Mn and Fe-2%Mn alloys for the various cooling rates used.

The transformation behaviour of Fe-1mass%Mn and Fe-2mass%Mn alloys during isochronal cooling from the austenisation temperature and as measured using Differential Scanning Calorimetry (DSC), can be analysed to derive information on the interface mobility by comparing the experimental results with the model discussed above.

Using all transformation data together and making appropriate assumptions on the grain size distribution, the parameter values describing the intrinsic interface mobility can be determined using a Simplex Downhill Method as a robust parameter estimation procedure. The activation energy is estimated as $E = 140$ kJ/mole, while the pre-exponential factor is estimated at $58$ mm mole/s. These values apply to both alloys. This value of the activation energy for the
interface mobility is comparable to that determined for recrystallisation in pure iron (Hillert, 1975). The pre-exponential factor however is considerably smaller.

**Interaction between Carbon Diffusion and Interface Mobility.**

The growth kinetics of the austenite to ferrite transformation in Fe-C alloys can not be modelled in exactly the same way as that in Fe-Mn alloys, as the transformation also necessarily involves carbon rearrangement. However, after making suitable modifications to the model, the same concept can be applied. This model will be briefly discussed here (see Krielaart and van der Zwaag (1995b) for full details).

Again the interface velocity is assumed to be equal to the product of the interface mobility and the difference of the chemical potential of iron on either side of the $\alpha/\gamma$ interface (cf. Eq. (3)). The chemical potential of iron on the ferritic side of the interface is calculated taking the carbon concentration either according to the equilibrium composition or the maximum solubility of carbon in ferrite at the transformation temperature concerned. The carbon is assumed to have a uniform distribution in the ferrite. This assumption is justified by the high carbon diffusivity in ferrite (Ågren, 1982). The chemical potential of iron in the austenitic state is calculated taking the local carbon concentration at the interface into account, thus establishing a mixed mode of growth control.

To calculate the austenite carbon concentration at the interface, the mass balance for carbon transport across the moving interface must be solved. This is basically the same approach as in diffusion controlled growth models, but in the present case the interface velocity is incorporated explicitly in the mass balance. For reasons of simplicity, one-dimensional growth of a flat interface will be considered only. The starting point is therefore the equation of continuity for mass transport. For one-dimensional growth of a flat interface, this reduces to:

$$\Delta c = \frac{\Delta J}{v},$$ (7)

where $\Delta c$ is the carbon pile-up at the interface due to the occurrence of non-equilibrium conditions while $\Delta J$ is the difference of the carbon mass-flux across the interface and carbon mass-flux from the interface into the bulk of the remaining austenite. The value of $v$ is evaluated according to Eq. (1). The values of $E$ and $M_0$ are taken according to the values as determined from the transformation kinetics in Fe-Mn alloys described above. The carbon mass-flux across the interface $J_{in}$ is given by:

$$J_{in} = \left(c_{\gamma}^{\gamma}_{\text{int.}} - c_{\alpha}^{\alpha}ight) v,$$ (8)

while the carbon mass-flux into the bulk of the remaining austenite $J_{out}$ is given by Fick's first law:

$$J_{out} = -D \left( \frac{dc}{dx} \right)_{\text{int.}},$$ (9)

where $D$ is the diffusion coefficient of carbon in austenite. Hence, the austenite carbon concentration at the interface $c_{\gamma}^{\gamma}_{\text{int.}}$ follows from:
\[ c_{\text{int}}(x + \Delta x, t + \Delta t) = c_{\text{int}}(x + \Delta x, t) + c_{\text{int}}(x, t) - c^\alpha + \frac{D}{v} \left( \frac{dc}{dx} \right)_{\text{int}}, \]  

(10)

where the interface has moved from position \( x \) to \( x + \Delta x \) during the time interval \( \Delta t \). Carbon volume diffusion is taken into account using Fick’s second law:

\[ \frac{\partial c}{\partial t} = \frac{\partial}{\partial x} \left( D \frac{\partial c}{\partial x} \right) \]  

(11)

The discrete form of these equations form a set of linear coupled equations that can be solved numerically. This set of equations takes the form of:

\[ \overline{A} \overrightarrow{c}(t + \Delta t) = \overrightarrow{c}_{\text{in}}, \]  

(12)

where \( \overrightarrow{c}(t + \Delta t) \) is the new carbon concentration profile and the matrix \( \overline{A} \) containing the coefficients describing both carbon diffusion and interface migration. The matrix \( \overline{A} \) is written as:

\[ \overline{A} = \begin{pmatrix} 1 & 0 & & & \frac{D}{\Delta x} & \frac{D}{\Delta x} & & & \frac{D}{\Delta x} & \frac{D}{\Delta x} & \frac{D}{\Delta x} \\ 0 & 1 & 0 & & \frac{\Delta x}{\Delta t} & 1 + \frac{\Delta x}{\Delta t} & \frac{\Delta x}{\Delta t} & \frac{\Delta x}{\Delta t} & \frac{\Delta x}{\Delta t} \\ 0 & 1 & 0 & & \frac{\Delta x}{\Delta t} & 1 + \frac{\Delta x}{\Delta t} & \frac{\Delta x}{\Delta t} & \frac{\Delta x}{\Delta t} & \frac{\Delta x}{\Delta t} \\ & & & & & & & & \vdots & \vdots & \vdots & \vdots \\ 0 & 1 & 0 & & \frac{\Delta x}{\Delta t} & 1 + \frac{\Delta x}{\Delta t} & \frac{\Delta x}{\Delta t} & \frac{\Delta x}{\Delta t} & \frac{\Delta x}{\Delta t} \\ & & & & & & & & & \frac{\Delta x}{\Delta t} & 1 + \frac{\Delta x}{\Delta t} & \frac{\Delta x}{\Delta t} & \frac{\Delta x}{\Delta t} \end{pmatrix} \]  

(13)

while the vector \( \overrightarrow{c}_{\text{in}} \) is given by:

\[ \overrightarrow{c}_{\text{in}} = \begin{pmatrix} c^\alpha \\ c^\alpha \\ c^\gamma(x_j + \Delta x, t) + c^\gamma(x_j, t) - c^\alpha \\ c^\gamma(x_{j+1} + \Delta x, t) \\ \vdots \\ c^\gamma(x_N, t) \end{pmatrix}, \]  

(14)

where \( j \) corresponds to the current interface position and \( c^\alpha \) and \( c^\gamma \) are the ferrite and austenite carbon concentrations respectively. The elements of the last row of Eq. (13) follow from the
assumption of symmetric growth of two opposite interfaces. The concentration dependency of $D$ is taken into account by evaluating $D$ according to the corresponding values of $c^\gamma$ using an expression due to Ågren (1986). As a result of the interaction between the interface mobility and carbon volume diffusion, as follows from Eq. (10), the austenite carbon concentration at the interface is not a constant but varies with the degree of transformation. The effect of carbon volume diffusion is that the driving force for interface migration $\Delta \mu_{Fe}$ is adjusted and hence the growth rate varies with time (and hence with the degree of transformation).

A typical example of the change of the interface concentration is shown in figure 3, which shows the carbon concentration profiles in a Fe-0.2% C alloy transforming at 1025 K assuming planar austenite grains with a half thickness of 25 mm.

As shown, the carbon concentration is always significantly less than that assumed in local equilibrium models, except at the final stages of the transformation where soft impingement occurs. In figure 4 the ferrite parabolic growth rate in an Fe-0.2% C alloy, at intermediate stages of transformation, is plotted as a function of the transformation temperature. In this figure the results for the present mixed mode growth model, the results of standard long-range diffusional growth models and experimental data are collected.

Recent EPMA measurements of the carbon concentrations at the former austenite-ferrite interface in partially transformed Fe-C samples (Krielaart et. al., 1994b) have indicated that the maximum carbon concentration indeed can be lower than that predicted by assuming local equilibrium. An example of such a measurement is given in figure 5. Details about the measurements of carbon concentration profile can be found Somers et. al (1990), Krielaart et. al. (1994b) and Silalahi et. al (1995). The numerical results can also be compared with experimental results concerning the interface positions as a function of time during isothermal transformation. An example is given in figure 5. The experimental results were obtained using quantitative image analysis (Silalahi et. al. (1995).

![Graph](image)

**Figure 3:** Carbon concentration profiles during the diffusional decomposition of an austenitic Fe-0.2mass% C alloy computed at various transformation times using a finite interface mobility. The isothermal transformation temperature is chosen as 1025 K and the half size of the austenite grain is chosen as 25 μm.

168
Figure 4: Parabolic growth rate coefficients a for a flat, disordered, interface as calculated from diffusion controlled growth theory. The alloy carbon composition is taken as 0.2mass%C. The results for a are given for the carbon diffusion coefficients according to the α/γ-equilibrium lines and according to the weighed average diffusion coefficient of the carbon in austenite (trived and Pound, 1967). For comparison, the slope of the linear part of the interface positions vs. the transformation time and the experimental results for the growth of ferrite grain boundary allotriomorphs, given by Bradley et. al. (1977) are given too.

Figure 5: Typical result of a carbon concentration profile across the α/γ-interface as determined using EPMA. The sample, containing approximately 0.2mass%C, is isothermally transformed at a temperature of 973 K. The transformation time is 5 s, yielding approximately 35% ferrite. The remaining austenite transformed into martensite upon quenching to room temperature.
Figure 6: Average position of a disordered $\alpha/\gamma$-interface at various transformation times and an isothermal transformation temperature of 973 K as measured using quantitative image analysis (see also Ref. [19]). The Fe-C alloy carbon composition is approximately 0.2mass% C.

Conclusions

From an analysis of the heat-effects occurring on cooling homogenised low Mn Fe-Mn alloys from the austenite one-phase region, the kinetics of the transformation $\gamma \rightarrow \alpha$ in such alloy systems is found to be determined by interface controlled growth. The transformation $\gamma \rightarrow \alpha$ in low Mn Fe-Mn alloys occurs entirely in the ferrite one-phase region. The experiments lead to the conclusion that the intrinsic $\alpha/\gamma$ interface mobility is not a negligible factor in the total transformation kinetics in plain-carbon steels.

While there are obvious differences in the predictions of kinetic models assuming diffusion controlled growth and the mixed mode model discussed in this work, they seem to describe the experimental growth kinetics data equally well. The mixed mode model, however, not only correctly predicts the growth rate but also the experimentally observed austenite carbon concentration at the interface. In principle, the mixed mode model can be used to predict the onset of pearlite formation as well as the ratio of peritectoid ferrite and pearlite at completed transformation and thus offers the possibility to predict some of the mechanical properties of the product. A further major advantage of the mixed mode model is the ability to simulate the effect of local variations of the interface mobility (due to interface pinning at precipitates, dislocations or specific crystallographic orientations) on the microscopic and macroscopic transformation rates. These effects will be reported elsewhere. The input for these further refinements of the model comes from in-situ TEM studies on the austenite to ferrite transformation in Fe-C alloys (Onink et al., 1994). These direct observations have shown that the movement of the interface is by no means as smoothly and continuously as predicted in the existing local equilibrium diffusional growth models and in the mixed mode growth model described here.
Acknowledgements

Financial support for this work was provided by Hoogovens Groep B.V., the Dutch Ministry of Economic Affairs (Innovative Development Program for Metals) and Stichting Technische Wetenschappen.

References