Diffusion processes in a migrating interface: The thick-interface model

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Abstract

During a solid/solid diffusive phase transformation from a parent β-phase to a product α-phase, dissipative processes due to diffusion in the bulk phases as well as rearrangement of the crystal lattice and diffusion in the interfacial region occur. A model has been developed that accounts for all the above-mentioned dissipative processes. By means of this thick-interface model it is possible to assign a finite thickness and a finite mobility to the interface. The evolution of the mole fraction profiles of the components in the bulk phases and in the interface can be simulated from a given initial state until a steady state or equilibrium is attained. Based on this theoretical framework the kinetics of the γ/α phase transformation in the Fe-rich Fe–Cr–Ni system is simulated. Starting from a certain initial composition the transformation kinetics exhibits the features of a massive or a bulk diffusion controlled transformation depending on temperature.

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1. Introduction and motivation

Rearrangement of atoms in the migrating interface, solute drag, trans-interface diffusion and spike formation are phenomena occurring to a smaller or larger extent in the interface and its nearest surroundings during diffusive and massive transformations. Several models of the interface were developed and have been used to describe the transformation kinetics. The task to model the kinetics of diffusive phase transformations becomes less complicated, if the dissipation of some of the above-mentioned processes is negligibly small compared to the remaining processes and can be neglected. Frequently it is assumed that the bulk phases are separated by an infinitely thin, i.e. sharp, interface. Diffusion processes in the interfacial region are then automatically out of the scope of these sharp interface models.

The simplest sharp interface model is used in the standard package DICTRA [1]. It is assumed that the transformation kinetics is controlled by diffusion processes in the bulk only and local equilibrium prevails at the interface. This implies that no Gibbs energy is dissipated due to lattice rearrangement. The simplifying assumption is equivalent to an infinite mobility of the interface. Such a model is suitable to describe the kinetics of bulk diffusion controlled diffusive phase transformations.

A sharp interface model, which considers the dissipation due to lattice rearrangement by a finite interface mobility, has been introduced by Svoboda et al. [2]. The evolution equations for the transformation kinetics are obtained by using the thermodynamic extremal principle (TEP), and the transformation kinetics can be simulated by means of this model in the full range – from bulk diffusion controlled to massive growth. In the frame of this model jumps at the interface of the chemical potentials of the interstitial components are zero and all of the substitutional components are equal [3]. It is evident that diffusion processes in the interface result in different contact conditions at the

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interface. As a consequence of these processes the jumps of the chemical potentials of the substitutional components need not be equal. This fact has been discussed, e.g. in Hillert’s review paper [4] and by Hillert and Rettenmayr [5].

A completely different sharp interface model is presented by Larsson et al. [6], who considered trans-interface diffusion instead of atomic rearrangement and Kirkendall shift instead of the interface migration.

The trans-interface diffusion, solute drag as well as the atomic rearrangement in the migrating interface are also incorporated into the thick-interface model for the phase transformation by Odqvist et al. [7]. All mentioned processes are also treated by the thick-interface model for the phase transformation by Svoboda et al. [8]. This model was applied to the simulations of massive transformation by Larsson et al. [6], who considered trans-interface diffusion instead of atomic rearrangement and Kirkendall effect. Then the total length of the system grows with the rate \( \dot{A} = v \). The values of \( A_k \) \((k = 1, \ldots, n - 1, n + 2, \ldots, m)\) and the thickness \( h \) of the interface are kept constant as well as the sum \( A \) as

\[
A = A_m + A_{n+1}.
\]

The mole fractions \( x_{ik} \), the fluxes \( j_{ik} \) and the chemical potentials \( \mu_{ik} \) are defined by the two subscripts \( i \) \((i = 1, \ldots, s)\) and \( k \) \((k = 1, \ldots, m)\), indicating the component and the location, respectively. The chemical composition of the interface is given by the local mole fractions of \( x_{ik} \equiv x_{in_k} \) and \( x_{m+k} \equiv x_{im+1} \), with a parabolic profile in the interface. As a closed system is investigated, the fluxes at the boundaries of the system are zero:

\[
\begin{align*}
  j_{ik} &= 0, \quad j_{im} = 0. 
\end{align*}
\]

For no sources and sinks for vacancies in the system, the vacancy fluxes can be neglected at every point in the system, leading to the constraint

\[
\sum_{i=1}^{m} j_{ik} = 0. 
\]

2.2. Mass balances

The mole fractions \( x_{ik} \) are constrained by

\[
\sum_{i=1}^{m} x_{ik} = 1 \quad (k = 1, \ldots, m), \quad \sum_{i=1}^{m} x_{ik} = 1, 
\]

and thus the total time derivatives are related by

\[
\begin{align*}
  \sum_{i=1}^{m} \dot{x}_{ik} &= 0 \quad (k = 1, \ldots, m), \quad \sum_{i=1}^{m} \dot{x}_{ik} = 0. 
\end{align*}
\]

The mass conservation relations hold in the individual regions characterized by \( A_k \) as

\[
\begin{align*}
  A_k \dot{x}_{ik} &= \Omega(j_{ik} - j_{ik}) \quad (k = 1, \ldots, n - 1, n + 2, \ldots, m), \\
  A_m \dot{x}_{ik} &= \Omega(j_{m-1} - j_{ik}), \quad A_{n+1} \dot{x}_{n+1} = \Omega(j_{m+1} - j_{m+1}) 
\end{align*}
\]

with the total time derivatives \( \dot{x}_{ik} = \frac{dx_{ik}}{dt} \) and \( \dot{x}_{ik} = \frac{dx_{ik}}{dt} \) since the variables \( x_{ik} \) and \( x_{im+1} \) are considered to be dependent only on time \( t \) (see Fig. 1 for introduction of the variables).

The parabolic mole fraction profile \( x_i(z, t) \) in the interface is expressed as

\[
x_i = x_{ik} - (x_{ik} - x_{im}) \frac{z}{h} + 2(x_{ik} - 2x_{ik} + x_{im}) \left( \frac{z}{h} \right)^2. 
\]

The material time derivative, being the rate of a quantity in a material point fixed to the lattice and moving with the velocity \( v \) from the right to the left, is given by

\[
\dot{x}_i = \frac{\partial x_i}{\partial t} - v \frac{\partial x_i}{\partial z}. 
\]
and coincides with the total time derivative. The material time derivative \( \dot{x}_i \) in the interface then follows with Eqs. (7) and (8) as

\[
\dot{x}_i(z) = \dot{x}_{iL} = \frac{2}{\Omega} \left( \frac{x_i}{h} \right)^2 \frac{z_0}{h} + \dot{x}_{iC} \left[ 1 - 4 \left( \frac{x_i}{h} \right)^2 \right]
\]

\[
+ \dot{x}_{iR} \left[ 2 \left( \frac{x_i}{h} \right)^2 \frac{z}{h} \right]
\]

\[
+ v \left[ 4(-x_{iL} + 2x_{iC} - x_{iR}) \frac{z}{h} + x_{iL} - x_{iR} \right].
\]

The flux in the interface is given by Eqs. (6) and (9) as

\[
j_i(z) = j_{iL} - \frac{1}{\Omega} \int_z \dot{x}_i(z')dz' = j_{iR} - \frac{\Delta x_i}{\Omega}
\]

\[
- \frac{1}{\Omega} \left\{ \dot{x}_{iL} \left[ \frac{5h}{24} \frac{z^2}{2h} + \frac{2z^3}{3h^2} \right]
\]

\[
+ \dot{x}_{iR} \left[ -\frac{h}{2} + \frac{z^2}{2h} + \frac{2z^3}{3h^2} \right] + \frac{\dot{x}_{iC} (h/3) + z - 4z^3}{3h^2}
\]

\[
+ v \left[ 2(-x_{iL} + 2x_{iC} - x_{iR}) \frac{z}{h} - \frac{1}{4} \right]
\]

\[
+ (x_{iL} - x_{iR}) \left( \frac{z}{h} + \frac{1}{2} \right) \right\}.
\]

Then the fluxes in the position \( z = 0 \) and \( z = h/2 \) (see Fig. 1) are given by

\[
j_{iC} = j(0) = j_{iL-1} - \frac{\Delta x_{iC}}{\Omega} \left[ \dot{x}_{iL} \frac{5h}{24} + \dot{x}_{iC} \frac{h}{3} \right]
\]

\[
- \dot{x}_{iR} \frac{h}{2} + v(x_{iL} - x_{iC})
\]

\[
(11)
\]

\[
j_{iR} = j(h/2) = j_{iL-1} - \frac{\Delta x_{iL}}{\Omega} \left[ \dot{x}_{iL} \frac{h}{6} + \dot{x}_{iC} \frac{2h}{3} + \dot{x}_{iR} \frac{h}{6} \right]
\]

\[
+ v(x_{iL} - x_{iR})
\]

\[
(12)
\]

The value of \( j_{i+1} \) is given by Eqs. (6), and (12) The kinetics of the system can be described by the values of independent kinetic variables represented by the fluxes \( j_{ik} \) \((i = 1, \ldots, s - 1, \ k = 1, \ldots, n - 1, \ n + 2, \ldots, m - 1)\), by the rates of the mole fractions \( \dot{x}_{iL}, \dot{x}_{iC}, \dot{x}_{iR} \)

\((i = 1, \ldots, s - 1)\) and by the interface velocity \( v \). The values of all other kinetic quantities can be obtained from Eqs. (2), (3), (5), and (6).

The TEP can be applied in a straightforward way to obtain the values of the kinetic variables. For the application of the principle it is necessary to express the rate \( \dot{G} \) of the total Gibbs energy \( G \) and the total dissipation \( Q \) in the system as functions of state variables and of independent kinetic variables and their rates, respectively. The actual values of state variables are given by initial conditions of \( x_{ik} (k = 1, \ldots, m)\) and \( x_{iC} (i = 1, \ldots, s)\) and by their integration in time by using Eqs. (6). The chemical potentials \( \mu_{ik} \) \((k = 1, \ldots, m), \mu_{iL} = \mu_{iC}, \mu_{iR}\) and \( \mu_{i+1} = \mu_{i+1} \) \((i = 1, \ldots, s)\) are given functions of \( x_{ik} \) \((k = 1, \ldots, m), \ x_{iC} \) \((i = 1, \ldots, s - 1)\) and of the temperature \( T \) and are considered to be known.

The part of the system containing the interface and its surroundings is of special concern. The fluxes \( j_{i-1} \) in the \( \alpha \)-phase, the rates of the mole fractions, \( \dot{x}_{iL}, \dot{x}_{iC} \) and \( \dot{x}_{iR} \), \((i = 1, \ldots, s - 1)\) and the interface velocity \( v \) can be chosen as the independent kinetic variables of this subsystem. Thus \( 4s - 3 \) kinetic variables describe the kinetics of the interface and its nearest surroundings. The values of these kinetic variables are provided by an interface module described later.

2.3. Rate of Gibbs energy

The Gibbs energy \( G \) of the system can be calculated as

\[
G = \frac{1}{\Omega} \sum_{i=1}^{s} \int_{z_i}^{z_{i+1}} x_i \mu_i dz
\]

\[
= \frac{1}{\Omega} \left[ \sum_{i=1}^{s} \sum_{k=1}^{m} A_{ik} x_{ik} + \sum_{i=1}^{s} \int_{h/2}^{h} x_i \mu_i dz \right]
\]

\[
= \frac{1}{\Omega} \left[ \sum_{i=1}^{s} \sum_{k=1}^{m} A_{ik} x_{ik} + \frac{h}{6} \sum_{i=1}^{s} (x_i \mu_i + 4x_{iC} \mu_{iC} + x_{iR} \mu_{iR}) \right],
\]

(13)
if Simpson’s rule is used for the calculation of the integral corresponding to the interface. The rate \( \dot{G} \) of the Gibbs energy can be calculated by

\[
\dot{G} = \frac{1}{6} \sum_{i=1}^{m} \left[ \sum_{j=1}^{m} D_{ij} \Delta x_{i} \mu_{jk} + \sum_{k=1}^{m} D_{ik} \Delta x_{i} \mu_{ik} \right] + \frac{h}{6} \sum_{i=1}^{m} \left( \dot{x}_{i} \mu_{ik} + 4 \dot{x}_{i} \mu_{jk} + \dot{x}_{i} \mu_{ik} \right).
\]  

(14)

Terms with rates of the chemical potentials vanish due to the Gibbs–Duhem equation, and only the thicknesses \( \Delta n \) and \( \Delta n+1 \) change with time as described above. By using Eqs. (6) and (14) \( \dot{G} \) can be written as

\[
\dot{G} = \sum_{i=1}^{m} \frac{V}{\Omega} (x_{i} \mu_{jk} - x_{i} \mu_{kj}) + \sum_{i=1}^{m} \left[ \sum_{j=1}^{m} (j_{i} - j_{i+1}) (\mu_{jk} - \mu_{ij}) + (j_{i} - j_{i+1}) (\mu_{jk} - \mu_{ij+1}) \right] + \frac{h}{6 \Omega} \sum_{i=1}^{m} \left[ \dot{x}_{i} (\mu_{ik} - \mu_{ij}) + 4 \dot{x}_{i} (\mu_{ik} - \mu_{ij+1}) + \dot{x}_{i} (\mu_{ik} - \mu_{ij+1}) \right].
\]  

(15)

Eq. (15) expresses \( \dot{G} \) as a linear form of the independent kinetic variables of the system.

2.4. Total Gibbs energy dissipation in the system

The Gibbs energy dissipation \( Q_k \) in region \( k \) \((k=1, \ldots, n-1, n+2, \ldots, m)\) is given by

\[
Q_k = \sum_{i=1}^{m} \frac{RT}{D_{xk}} \int_{a_i}^{b_i} j^2 \, dz \approx \sum_{i=1}^{m} \frac{RT \Omega A_k}{2 D_{xk}} (j_{i-1}^2 + j_i^2)
\]  

(16)

if Eq. (2) and the trapezoidal integral rule are used. The quantity \( D \) denotes the bulk diffusion coefficient of component \( i \) in the \( \alpha \)-phase, \( D^\alpha_k \), for \( k=1, \ldots, n-1 \), or in the \( \beta \)-phase, \( D^\beta_k \), for \( k=n+2, \ldots, m \). The trapezoidal integration rule works nearly exactly for not too different values of \( j_{i-1} \) and \( j_i \) (which is usually the case). Some inaccuracy can be expected at the ends of the system due to the validity of conditions (2). The application of, in this case exact, Simpson’s rule would, however, lead to a much more complicated solution procedure for the fluxes \( j_{i_k} \) (see later the analytical solution given by Eqs. (27) and (28)).

Similarly one can write the Gibbs energy dissipation \( Q_n \) and \( Q_{n+1} \) in regions \( n \) and \( n+1 \) following as

\[
Q_n = \sum_{i=1}^{m} \frac{RT \Omega A_n}{2 D_{xnl}} (j_{i-1}^2 + j_i^2) + \frac{RT \Omega A_n}{2 D_{xnl}} \left[ \left( \sum_{i=1}^{m_1} j_{i-1} \right)^2 + \left( \sum_{i=1}^{m_1} j_i \right)^2 \right].
\]  

(17)

\[
Q_{n+1} = \sum_{i=1}^{m} \frac{RT \Omega A_{n+1}}{2 D_{xnr}} (j_{i-1}^2 + j_i^2) + \frac{RT \Omega A_{n+1}}{2 D_{xnr}} \left[ \left( \sum_{i=1}^{m_1} j_{i-1} \right)^2 + \left( \sum_{i=1}^{m_1} j_i \right)^2 \right].
\]  

(18)

If we assume that the diffusion coefficient changes gradually from the value \( D^\alpha \) at the left end of the interface over the value \( D^\beta \) in the centre of the interface to the value \( D^\gamma \) at the right end of the interface, then the Gibbs energy dissipation \( Q_{if} \) in the interface can be calculated by applying Simpson’s rule as

\[
Q_{if} = \frac{RT \Omega h}{6} \sum_{i=1}^{m} \left[ \left( \sum_{j=1}^{m_1} j_{i-1} \right)^2 + \left( \sum_{j=1}^{m_1} j_i \right)^2 + \left( \sum_{j=1}^{m_1} j_{i+1} \right)^2 \right].
\]  

(19)

The total dissipation in the system is given by

\[
Q = \sum_{k=1}^{m} Q_k + Q_{if} + \frac{\dot{v}^2}{M}
\]  

(20)

with \( M \) being the interface mobility.

The corresponding expressions for \( j_{iL}, j_{iC} \), and \( j_{iR} \) given by Eqs. (6), (11), and (12), must be inserted into Eqs. (16)–(20). Then the total dissipation in the system \( Q \) becomes a positive definite quadratic form of the independent kinetic variables.

3. Evolution equations and their solution

3.1. General evolution equations

Let us denote by \( \dot{q}_l \) \((l=1, \ldots, m(s-1)+1)\) all independent kinetic variables being the fluxes \( j_{i_k} \) \((i=1, \ldots, s-1, k=1, \ldots, n-1, n+2, \ldots, m-1)\), the rates of the mole fractions \( \dot{x}_{i}, \dot{x}_{iC}, \dot{x}_{iR} \) \((i=1, \ldots, s-1)\) and the interface velocity \( v \). Then the rate \( \dot{G} \) of the total Gibbs energy represents a linear form in \( \dot{q}_l \) and the total Gibbs energy dissipation \( Q \) a quadratic, positive definite form in \( \dot{q}_l \). The TEP provides the evolution equations for the independent kinetic variables \([9]\) as

\[
\frac{1}{2} \frac{\partial Q}{\partial \dot{q}_l} = - \frac{\partial \dot{G}}{\partial \dot{q}_l}, \quad (l=1, \ldots, m(s-1)+1)
\]  

(21)

being a set of linear equations for \( \dot{q}_l \). The set of Eqs. (21) can be rewritten as

\[
\sum_{k=1}^{m(s-1)+1} A_{kl} \dot{q}_k = F_l, \quad (l=1, \ldots, m(s-1)+1)
\]  

(22)

with the coefficients

\[
A_{kl} = \frac{1}{2} \frac{\partial^2 Q}{\partial \dot{q}_k \partial \dot{q}_l}
\]  

(23)
The quantities $A_{kl}$ and $F_i$ are independent of $\dot{q}_i$ $(i = 1, \ldots, n(s-1)+1)$ and can easily be produced by mathematics processors as MAPLE 8 (http://www.scientific.de/maple.html).

As the actual state of the system is given by the state variables, represented by the values of $x_{ik}$, $(i = 1, \ldots, s-1, k = 1, \ldots, m)$, $x_{ic}$, $x_{ir}$ ($i = 1, \ldots, s-1$) and by the values of $A_k$, $(k = 1, \ldots, m)$, the rates of the state variables coincide either with the kinetic variables $\dot{q}_i$ or they are related by Eqs. (6) and (12) and by

$$\dot{A}_n = v, \quad \dot{A}_{n+1} = -v, \quad \dot{A}_k = 0 \quad (k = 1, \ldots, n-1, n+2, \ldots, m).$$

It should be noted that the state variables evolve in such a way that the total amount of moles $N_i$ of all components $i$, $(i = 1, \ldots, s-1)$ remains constant, i.e.

$$\frac{1}{\Omega} \left( \sum_{k=1}^{m} A_k x_{ik} + \frac{h}{6} (x_{il} + 4x_{ic} + x_{ir}) \right) = N_i = \text{const.,}$$

in accordance with the assumption of a closed system.

### 3.2. Solution of evolution equations

A subset of the kinetic variables, namely $j_{ik}$ $(i = 1, \ldots, s-1, k = 1, \ldots, n-2, n+2, \ldots, m-1)$, can be determined analytically in the same way as presented in Ref. [2], resulting in

$$j_{ik} = -B_k \left( \mu_{ik+1} - \mu_{ik} - \sum_{j=1}^{s} B_{jk} (\mu_{jik+1} - \mu_{jik}) \right)$$

with

$$B_k = \frac{2}{RT\Omega} \left( \frac{A_k^{-1}}{x_{ik} A_k + \frac{4k+1}{k+1} A_{k+1}^{-1}} \right).$$

Then the set of Eqs. (22) reduces to a subset of linear equations of dimension $4s-3$ for $j_{in-1}$, $\dot{x}_{il}$, $\dot{x}_{ic}$, $\dot{x}_{ir}$, $(i = 1, \ldots, s-1)$ and $v$. The respective coefficients as subsets of $A_{kl}$ and $F_i$ are calculated by applying MAPLE 8 (http://www.scientific.de/maple.html) and exported into a FORTRAN code. The system of linear equations for the kinetic variables $j_{in-1}$, $\dot{x}_{il}$, $\dot{x}_{ic}$, $\dot{x}_{ir}$, $(i = 1, \ldots, s-1)$ and $v$ is solved numerically. This procedure represents the interface module mentioned at the end of Section 2.3. The module takes $A_{n-1}$, $A_n$, $A_{n+1}$, $A_{n+2}$, $x_{in-1}$, $x_{in+2}$, $x_{il}$, $x_{ic}$ and $x_{ir}$ $(i = 1, \ldots, s-1)$, the diffusion coefficients $D_i$, $D_j$, $D_k$, $(i = 1, \ldots, s)$ and the interface mobility $M$ as input quantities and provides the values of the kinetic variables $j_{in-1}$, $\dot{x}_{il}$, $\dot{x}_{ic}$, $\dot{x}_{ir}$, $(i = 1, \ldots, s-1)$ and $v$ as output quantities.

To ensure a sufficient accuracy of simulations a dense mesh near the interface must be chosen. As the interface moves relatively to the nodal points, this fact provokes a frequent elimination or addition of nodes right and left to the interface and may cause numerical instability. Thus, similarly as in Ref. [2], it is advantageous to keep the positions of the nodal points fixed. Therefore, we switch from moving nodal points to fixed nodal points and, thus, the rates of quantities at these points are described by partial time derivatives. The only exceptions are the nodal points at the ends of the system, which must remain moving. Then it holds that

$$\frac{\partial A_k}{\partial t} = 0, \quad (k = 2, \ldots, m-1), \quad \frac{\partial A_{n+2}}{\partial t} = v \quad \text{and} \quad \frac{\partial A_m}{\partial t} = -v,$$

and only the nodal points immediate to the ends must be added or eliminated if $A_1$ gets too large or $A_m$ gets too small.

For a continuous profile of the mole fractions the partial time derivatives can be calculated from the material time derivatives by means of formula (8) as

$$\frac{\partial x_i}{\partial t} = \dot{x}_i + v \frac{\partial x_i}{\partial z}.$$  

In a discrete description, using a net of non-equidistant nodal points, however, the partial derivatives must be calculated numerically. This doing may cause inaccuracies so that the total amounts of moles $N_i$ from Eq. (26) are not conserved. To guarantee the conservation, we recommend using the following set of relations valid for a general discretization, which turns into Eq. (30) for infinitesimally fine discretization:

$$v > 0: \frac{\partial x_{ik}}{\partial t} = \dot{x}_{ik} + v \frac{x_{ik+1} - x_{ik}}{A_k},$$

(i = 1, \ldots, s, k = 1, \ldots, n-1, n+2, \ldots, m-1),

$$\frac{\partial x_{in+1}}{\partial t} = \dot{x}_{in+1} + v \frac{x_{in+2} - x_{in+1}}{A_{n+1} + h/6},$$

(i = 1, \ldots, s),

$$\frac{\partial x_{im}}{\partial t} = \dot{x}_{im},$$

(i = 1, \ldots, s),

$$v < 0: \frac{\partial x_{ik}}{\partial t} = \dot{x}_{ik},$$

(i = 1, \ldots, s),

$$\frac{\partial x_{in+1}}{\partial t} = \dot{x}_{in+1} + v \frac{x_{in+2} - x_{in+1}}{A_{n+1} + h/6},$$

(i = 1, \ldots, s),

The $h/6$ term in Eqs. (33) and (37) stems from the application of Simpson’s rule in Eq. (26).
such structure. The chemical potentials in the undercooled liquid seems to be a good approximation of assumed as thin layers of amorphous structure, and the Usually incoherent interfaces at high temperature are dynamic properties in the centre of the interface (see Fig. 1, 4780 J. Svoboda et al. / Acta Materialia 59 (2011) 4775–4786

The partial time derivatives of Eq. (26) reads after switching to fixed nodal points as

\[ v(x_i - x_{im+1}) + \sum_{k=1}^{n-1} \Delta_t \dot{x}_{ik} + \sum_{k=n+2}^{m-1} \Delta_t \dot{x}_{ik} + \Delta_t \dot{x}_{im} + \Delta_t \dot{x}_{im+1} \\
+ \Delta_t \dot{x}_{im} + \frac{h}{6} (4 \dot{x}_{iC} + \dot{x}_{iC+1}) = 0. \]  (39)

The values of the thermally activated diffusion coefficients of the components in the product \( \alpha \)-phase, in the interface and in the parent \( \gamma \)-phase and the value of the thermally activated interface mobility \( M \), are specified in Table 1. For the interface mobility \( M \) the value of Krielaart [15] is chosen, which is approximately 500 times below the value estimated in pure Fe in Ref. [16]. As the solubility of Ni and Cr in the interface region is considerably higher than in the \( \alpha \) and \( \gamma \) bulk phases for all temperatures investigated, Ni and Cr atoms segregate at the interface and are dragged during the phase transformation. The typical steady state mole fraction profiles in the interface and its nearest surroundings, corresponding to a massive transformation [17], are observed at \( T = 1055 \) K. The mole fraction profiles of Ni at different times are plotted in Fig. 3a, and it can be concluded that the interface migrates with a constant velocity. The mole fraction peaks, indicating the position of the interface, move equal distances from the left to the right for equal time periods. It is not possible to get an idea about the segregation profiles in the interface from Fig. 3a as the interface is thin compared to the shown spatial range and the maximum segregation level exceeds the plotted \( x_{Ni} \) range. However, a closer view to the evolution of the mole fractions in the interface and its nearest surroundings can be provided, if the profiles for different instants are shifted so that the centre of the interface always coincides.

The deviation from the initial composition around \( z = 0 \) in Fig. 3a follows from the mass balance. The Ni spike and the Cr spike evolve in the interface and thus Ni and Cr diffuse from the \( \alpha \)-phase into the interface. During the transformation the deviation from the initial composition in the \( \alpha \)-phase decreases gradually. By this deviation from the initial composition during the initial stages of the phase transformation it is demonstrated that we do not start from a steady state profile, but we let the profile evolve until steady state or equilibrium is attained.

Now one can easily show that the insertion of Eqs. (31)–(38) into Eq. (40) yields Eq. (39), which proves the mass conservation for switching to fixed nodal points.

4. Results of simulations and their discussion

By means of the derived evolution equations the kinetics of the \( \gamma \) to \( \alpha \) transformation in the Fe-rich Fe–Cr–Ni system is simulated. The length of the system is set to 0.5 \( \mu \)m. The thickness of the interface is generally considered to be one or two interatomic distances and thus \( h = 0.3 \) nm is chosen. The molar volume is given by \( \Omega = 7.3 \times 10^{-6} \) m\(^3\) mol\(^{-1}\) and assumed to be independent of chemical composition and phase. The initial chemical composition is set to \( x_{Cr} = 0.01 \) and \( x_{Ni} = 0.015 \) in both phases. Simulations are performed for temperatures, \( T = 1055 \) K, 1060 K, 1061 K, 1062 K, 1065 K and 1080 K. The chemical potentials \( \mu_i \) are calculated according to the thermodynamic assessments [10–12]. Similar to the work presented in Ref. [8] we assume that the thermodynamic properties in the centre of the interface (see Fig. 1, \( z = 0 \)) can be approximated by the thermodynamic properties of the liquid phase, however, extrapolated to its value corresponding to the temperature used in the calculations. Usually incoherent interfaces at high temperature are assumed as thin layers of amorphous structure, and the undercooled liquid seems to be a good approximation of such structure. The chemical potentials in the \( \alpha \)-phase and in the \( \gamma \)-phases as well as in the interface are weighted by cubic Hermite interpolation splines [8]. The diffusion coefficients in the interface are also interpolated by Hermite polynomials as described in Ref. [8].

The relevant part of the phase diagram is the Fe-rich corner in the Fe–Cr–Ni system, where the \( \gamma/\alpha \) phase transformation occurs. The \( \alpha/(\alpha + \gamma) \) phase boundaries are computed by minimizing the Gibbs energy of the system and are depicted in Fig. 2 for all chosen temperatures. The \( \gamma/\alpha \) phase transformation occurs for the temperatures 1055 K and 1060 K in the \( \alpha \)-single-phase region and for higher temperatures the transformation occurs in the \((\alpha + \gamma)\)-two phase region.

![Fig. 2. Phase boundaries between the \( \alpha \)-single phase region and the \((\alpha + \gamma) \) region for certain temperatures. The initial composition is marked by a circle.](image-url)
The Ni profiles are presented in Fig. 3b. The shape of the profile does not change with time, and an extremely thin spike (highlighted in grey) is observed in the parent phase. The Cr profiles are shown in Fig. 3c. Compared to the Ni profiles, the Cr spike in the parent phase is lower and its half width is larger due to a higher diffusivity of Cr in the $\gamma$-phase. Of course, one could argue that it has no sense to talk about spike thicknesses of the order of magnitude of 1/100 of an interatomic distance. However, if one assumes the 1-D case and makes a statistics from a sufficiently large area of the interface, corresponding to a sufficiently large number of atoms in the spike, then the reasoning makes sense.

A detailed analysis of the transformation was performed for $T = 1060$ K, i.e. for a temperature for which the initial composition almost coincides with the $\alpha/(\alpha + \gamma)$ phase boundary, as can be seen in Fig. 2. In this exceptional case the total length of the system is increased to 2 $\mu$m, so that the interface velocity can be stabilized. In Fig. 4 the mole fraction profiles of Ni are plotted in the same way as in Fig. 3b. One can clearly observe that the profile approaches a steady state. However, the system requires a transition time period from the start of the transformation to the steady state being orders of magnitude higher at $T = 1060$ K compared to $T = 1055$ K. The profiles at $t = 1000$ s (solid circles) and at $t = 2000$ s (solid line) cannot be distinguished from each other, indicating that steady state is reached.

In this context the difference between the seminal work by Cahn [18] and the present model should be expressed. Cahn assumes in his model that the profile of the chemical potential of the dragged component in the interface, the diffusion coefficient of the dragged component and the velocity of migration are known. Then Cahn solved the steady-state diffusion equation in the migrating interface for zero diffusive flux at the contact of the product phase with the interface, obtained the concentration profile of the dragged component and calculated the total drag force. The resulting interface velocity followed then from the balance equation of forces acting at the interface. This equation is an implicit equation for the interface velocity, which can be resolved analytically only for special cases.

In our model we also assume that the chemical potential of the dragged component in the interface and the diffusion coefficient of the dragged component are known. We, however, expect a parabolic concentration profile in the

### Table 1

Diffusion coefficients in the Fe-Cr-Ni system and grain boundary diffusivity as an approximation for the diffusivity in the interface and the interface mobility. $Q_A$ is the activation energy.

<table>
<thead>
<tr>
<th>Diffusion coefficient</th>
<th>$D_0$ (m$^2$ s$^{-1}$)</th>
<th>$Q_A$ (J mol$^{-1}$)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr in $\alpha$ phase</td>
<td>$3.2 \times 10^{-4}$</td>
<td>$2.4 \times 10^5$</td>
<td>[13]</td>
</tr>
<tr>
<td>Ni in $\alpha$ phase</td>
<td>$4.8 \times 10^{-5}$</td>
<td>$2.4 \times 10^5$</td>
<td>[13]</td>
</tr>
<tr>
<td>Fe in $\alpha$ phase</td>
<td>$1.6 \times 10^{-4}$</td>
<td>$2.4 \times 10^5$</td>
<td>[13]</td>
</tr>
<tr>
<td>Cr in interface</td>
<td>$2.2 \times 10^{-4}$</td>
<td>$1.55 \times 10^5$</td>
<td>[14]</td>
</tr>
<tr>
<td>Ni in interface</td>
<td>$0.22 \times 10^{-4}$</td>
<td>$1.55 \times 10^5$</td>
<td>[14]</td>
</tr>
<tr>
<td>Fe in interface</td>
<td>$1.1 \times 10^{-4}$</td>
<td>$1.55 \times 10^5$</td>
<td>[14]</td>
</tr>
<tr>
<td>Cr in $\gamma$ phase</td>
<td>$3.5 \times 10^{-4}$</td>
<td>$2.86 \times 10^5$</td>
<td>[13]</td>
</tr>
<tr>
<td>Ni in $\gamma$ phase</td>
<td>$3.5 \times 10^{-5}$</td>
<td>$2.86 \times 10^5$</td>
<td>[13]</td>
</tr>
<tr>
<td>Fe in $\gamma$ phase</td>
<td>$7 \times 10^{-5}$</td>
<td>$2.86 \times 10^5$</td>
<td>[13]</td>
</tr>
<tr>
<td>Interface mobility</td>
<td>$M_0$ (m$^2$ s$^{-1}$)</td>
<td>$Q_A$ (J mol$^{-1}$)</td>
<td></td>
</tr>
<tr>
<td>Interface</td>
<td>$4.1 \times 10^{-7}$</td>
<td>$1.4 \times 10^5$</td>
<td>[15]</td>
</tr>
</tbody>
</table>

Fig. 3. Mole fraction profiles for different instants at $T = 1055$ K. Thin vertical lines indicate the position of the interface. Mole fraction spikes in the parent phase in front of the migrating interface are highlighted in grey. (a) Profiles of the Ni-mole fraction in the whole system. (b) Profiles of the Ni-mole fraction in the interface and its vicinity. (c) Profiles of the Cr-mole fraction in the interface and its vicinity.
interface (the height of the parabola is given by its value in the centre of the interface) and allow the diffusive interaction of the interface with both adjacent crystals (our solution is not limited to zero diffusive flux at the contact of the product phase with the interface). We start with a certain profile of the dragged component in the system. The rate of change of the profile and the actual interface velocity are determined from TEP. Thus, no implicit equation for the interface velocity must be solved. Under steady-state conditions, corresponding to the massive transformation, the concentration profile and the interface velocity approach very quickly their stationary values.

The features of the transformation kinetics are also studied at $T = 1061$ K. The composition lies already in the two-phase region at this temperature. The mole fraction profiles at different instants are plotted in Fig. 5a. The characteristics of the transformation seem to be that of a massive transformation. However, the Ni-mole fraction in the product phase is slightly different to the Ni-mole fraction in the parent phase far from the interface. This is a clear difference to the result observed at $T = 1055$ K (see Fig. 3a), where these mole fractions do not deviate from each other provided that the boundary of the system is sufficiently far away. A closer view at the profiles in the interface and its vicinity exhibits also some slight deviations from the character of a massive transformation (see Fig. 5b) as the half thickness of the spike gradually increases.

At 1065 K the mentioned effects are further increased compared to 1061 K, see Fig. 6. Finally, it can be stated that the transition from the massive transformation to a diffusion transformation occurs in a continuous manner with increasing transformation temperature.

Finally, the transformation kinetics is simulated for a temperature $T = 1080$ K, see Fig. 7. The kinetics is evidently controlled by bulk diffusion.

The evolution of the interface velocities for different temperatures $T = 1055$ K, 1060 K, 1061 K, 1062 K, 1065 K and 1080 K is plotted in Fig. 8. For $T = 1055$ K the interface velocity quickly stabilizes at a certain value (Fig. 8a). A constant interface velocity indicates that the transformation occurs in the massive mode characterized by identical chemical compositions in the product $\alpha$-phase near the interface (described by $x_{im}$) and in the parent $\gamma$-phase (described by $x_{im}$) far from the interface. The velocity stabilizes more slowly at temperature $T = 1060$ K (Fig. 8b) compared to 1055 K (Fig. 8a), but a steady state is finally reached and the transformation can be considered as a massive one. For $T = 1061$ K, 1062 K and 1065 K the interface velocity, depicted in Fig. 8c, decreases monotonously and eventually goes to zero when equilibrium is reached. This is the case for $T = 1080$ K – see Fig. 8d. The velocity plotted vs. $t^{-1/2}$ demonstrates even clearer whether a steady state or a constant velocity is attained after a certain period of transformation (small $t^{-1/2}$ values) or if the equilibrium state will eventually be reached (Fig. 8d). Whereas the transformations at 1055 K and 1060 K yield to a constant velocity, the interface velocity corresponding to the transformation in the two-phase region ($T \geq 1061$K) gradually decreases (Fig. 8e).

Equivalent to the jump $[[\alpha]]$ of a quantity $\alpha$ at the sharp interface – described by the difference $d^\alpha - d^\alpha$ with the
superscript “o” pointing to the parent phase and “m” to the product phase – the difference of a quantity \( \Delta a \) at the migrating thick interface is defined by \( \Delta a = a^{\text{o/m}} - a^{\text{o/I}} \), where \( a^{\text{o/I}} \) is the value of \( a \) at the boundary of the old phase with the interface and \( a^{\text{o/m}} \) is the value of \( a \) at the boundary of the new phase with the interface. The sharp interface model strictly enforces that the jumps of the chemical potentials across the sharp interface must be identical for all substitutional components [2,3]. In contrast to the sharp interface model, dissipation due to diffusion processes in the interface is considered in the present model. This enforces to change the contact conditions at the interface, expressed by differences of the chemical potentials \( \Delta \mu_i \) of the components across the interface. The differences of the chemical potentials \( \Delta \mu_i \) deviate from being equal. Evolution of \( \Delta \mu_i \) of individual components are presented in Fig. 9a for \( T = 1055 \) K, in Fig. 9b for \( T = 1060 \) K and in Fig. 9c for \( T = 1080 \) K.

These non-equal differences of chemical potentials cause the composition for the massive/diffusive transformation transition not to be identical with the one-phase/two-phase region boundary. According to experimental data the massive transformation may also occur in the two-phase region in certain alloys [19,20]. Borgenstam and Hillert [19] found that the massive transformation from \( \gamma \rightarrow \gamma_m \) in the Fe–Ni system is well inside the two-phase region for temperatures below 1023 K and remains in the \( \alpha \)-single-phase region for temperatures above 1023 K.

In the current simulation performed at 1055 K for a similar system a massive transformation in the two-phase region has not been obtained, too. From a qualitative point of view the massive transformation can enter the two-phase region if the differences of chemical potentials across interface are not equal for all components; just this occurs in our case – see Fig. 9. The change in temperature may affect the relations between the diffusion coefficients and interface mobility due to different activation energies of the processes and so the difference in chemical potentials can be influenced. That is why the occurrence of the massive transformation in the two-phase region can be dependent on temperature. However, this extensive problem deserves a detailed separate analysis, which would significantly complicate the present paper.

5. Final comments

The reader may be interested in the comparison of the present approach with the existing approaches based on the Ginzburg–Landau (Allen–Cahn) and Cahn–Hilliard phase field theories described for example in Ref. [21]. The phase field method represents one of the possibilities, how the thick interface can be treated. This requires introducing an order parameter being a continuous function in space and time, the value of which indicates the correspondence to one of the phases in the system or to the interface. The rate of the order parameter is assumed to be proportional to the conjugate driving force given by the variational derivative of the total Gibbs energy functional with respect to the order parameter. The total Gibbs energy functional must involve a squared gradient term of the order parameter to ensure a required thickness of the interface. Cahn has shown (see e.g. Ref. [21]) that by proper
choice of the Gibbs energy functional and by proper choice of the inner product used in the variational derivative of the Gibbs energy functional, various already known evolution equations for field variables can be obtained. This mathematically motivated approach provides a deeper insight into the understanding of the problem and raises hopes in general principles for microstructure evolution.

Our approach is based on the application of the thermodynamic extremal principle (TEP) originally formulated by Onsager in 1931 [22]. From the view of physics the TEP represents a strong formulation of the second law of thermodynamics. The path of the evolution of the system is selected unambiguously as it corresponds to the constrained maximum of the entropy production rate (dissipation). A general formulation of the TEP was given by Ziegler in his book [23], stating that the dissipation has to be maximized with the constraint that the dissipation must be identical to the negative rate of Gibbs energy. This formulation was adopted and reformulated for discrete parameters by Svoboda et al. in 1991, [24] and later on
extended to a generalized tool [9] with applications in several areas of micromechanics. Specifically, we refer to a rigorous derivation of the diffusion equations for systems with non-ideal sources and sinks for vacancies [25,26].

If a system is described by field variables (like concentration profiles), TEP can be used in its variational form (as it was originally formulated by Onsager) and reproduces the evolution equations for the field variables. Of course, one of the field variables can be the order parameter (an according study is in preparation). Thus, both TEP as well as the Cahn variational principle (see e.g. Ref. [21]) can be used for the description of system evolution by field variables and provide the complete set of evolution equations. However, there exists at least one substantial difference between both principles: Cahn’s extremal principle performs variations with respect to state parameters and TEP performs variations with respect to rates of state parameters or generalized fluxes related to the rates of state parameters.

In our model of the thick interface an optimized set of discrete parameters instead of field variables is selected for the description of the system. The derivation of the evolution equations can be performed in a straightforward way by means of TEP formulated in terms of discrete parameters [9,24]. However, dealing with discrete parameters would make it necessary to modify the Cahn variational principle. Our approach allows choosing the interface thickness as a fixed quantity, and the interface itself can be considered as spatially weighted combination of three phases. No order parameters need to be introduced and consequently its squared gradient term does not enter the total Gibbs energy. Such an approach allows also characterizing the concentration profile in the interface, e.g. by a parabolic shape function, for which compared to the sharp interface approach only one additional parameter is necessary.

The reader might ask why such a complicated solution procedure must be followed, if only two processes are involved – diffusion of the components and migration of the interface with finite mobility – having in mind that the phase field method provides simple equations and a robust method for their solution on a fixed equidistant grid.

Let us check the possibility of application of the phase field method for the problem at hand. We need to work with a system of total length of at least $10^{-7}$ m and times up to seconds. To obtain a sufficiently accurate concentration spike in front of the migrating interface, the grid distance must be of the order of $10^{-11}$ m. Thus, an extremely fine grid with at least $10^4$ nodal points is necessary. Furthermore, one must take into account that the diffusion coefficient in the interface is several orders of magnitude higher than in the bulk. Both these facts cause extreme complications with respect to the stability of the numerical solution of the diffusion equation for required times. In addition, the interface mobility must also be taken sufficiently high to ensure an interface migration controlled by the diffusion in the interface. Consequently, the kinetic coefficient in the evolution equation for the order parameter must also be high. All these facts certainly increase the complications with stability of the numerical solution on a very fine grid. To sum up, one cannot expect that the present problem is solvable by means of the phase field method with existing computers in reasonable computational times.

The present TEP-based model avoids the problems with the stability of the numerical solution by several subtle measures:
• Solving the diffusion equation in the interface by using a parabolic shape function with one evolving parameter (the height of the profile in the centre of the interface). The concept is open also for a more flexible shape functions, e.g. polynomials of fourth order, by introducing more evolving parameters.

• Using a non-equidistant grid with highest density of nodal points in the location of the concentration spike in front of the migrating interface. There the diffusion coefficients obtain small values corresponding to the bulk and cause no numerical difficulty.

• A grid moving with the interface.

• Incorporating the finite mobility of the interface by one term in the total dissipation. This allows varying the mobility within a wide range without loss of stability of the numerical solution.

6. Summary

A thick-interface model for solid-solid diffusive phase transformation is presented. The model accounts for dissipative processes due to diffusion in the bulk phases and due to rearrangement of the crystal lattice and diffusion in the interfacial region. The mole fraction profiles of all components are assumed to be parabolic ones in the interface and described by one parameter for each component, i.e. the mole fraction in the centre of the interface. The actual state of the system is described by a certain number of variables whose evolution equations are derived by application of the thermodynamic extremal principle (TEP). The processes in the thick interface are treated by an interface module, which implicitly determines the contact conditions at the migrating interface.

The model is used for extensive simulations of the diffusive and massive transformations in the Fe-rich Fe–Cr–Ni system. Equal jumps of chemical potentials of all substitutional components are obtained by sharp interface models and, thus the massive transformation analysed in the sharp interface approach can occur only in the one-phase region. By means of the current, thick-interface model, however, the differences of the chemical potentials of the components at the migrating interface can have different values. Therefore, massive transformation in the two-phase region could be predicted with this thick-interface model. The gradual change from a massive to a bulk diffusion controlled phase transformation depending on composition and temperature is demonstrated.

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