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A Model for the Austenite-Ferrite Phase Transition in Steel Including Misfit Stress

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Abstract

We present a thermodynamically consistent model to describe the austenite-ferrite phase transition in steel. We consider the influence of the mechanical displacement field due to eigenstrains caused by volumetric expansions. The model equations are derived in a systematical framework. They are based on the conservation laws for mass and momentum and the second law of thermodynamics. By means of numerical computations for a simplified interface-controlled model, we examine the influence of the mechanical contributions to the transformation kinetics and the equilibrium states.

1 Introduction

Steel is one of the most widely used materials. By alloying, heat- and thermomechanical treatment a broad spectrum of properties can be obtained. The microstructure and the distribution of different phases such as ferrite, austenite, martensite or pearlite are of great importance, due to the fact that they each possess different hardnesses and other mechanical properties, see e. g. [12].

In this study, we examine the phase transition from austenite (γ-iron) to ferrite (α-iron) as a preliminary stage to the modelling of the formation of pearlite, which is a lamellar mixture of ferrite and cementite – a metastable compound Fe_3C.

The phases austenite and ferrite are characterised by different crystal structures. Important for their constitution is the so called sublattice model. The iron atoms form a host lattice, which has a body centred cubic (bcc) structure in the α-phase and a face centred cubic (fcc) unit cell in the γ-phase. The carbon atoms are interstitially dissolved on a sublattice, which is formed by the octahedral sites. The number of sublattice sites is different in ferrite and austenite. In α-iron, there are three times as many sublattice sites as iron atoms, whereas in γ-iron both lattices have an equal number of lattice sites. Empty sublattice sites are a carrier of energy and entropy and have to be considered. These vacancies are introduced in the model as a massless constituent.

Two processes that determine the γ/α-phase transition are the diffusion of carbon through the austenite and the lattice transformation of the iron. If one of these processes dominates the other, special cases can be considered. The transformation behaviour is called diffusion-controlled, if the carbon diffusion is dominating. If the second process determines the growth rate of the new phase, then one refers to the interface-controlled mode and a homogeneous carbon distribution can be assumed. Furthermore, mechanical stresses and strains affect the phase transition. Because of the different crystal structure, ferrite has a larger molar volume than austenite. In addition, the carbon atoms have a larger diameter than the sublattice sites offer in space. Therefore, dissolved carbon causes an expansion of the iron lattice. The changes of the volume during the γ/α-phase transition due to these effects cause eigenstrains, which accelerate or decelerate the growth of the ferrite phase. The model presented here accounts for the local mechanical fields caused by the volumetric expansions.

Probably one of the earliest studies considering the diffusion-controlled case has been done by Zener [13] as early as 1949. In a work by Wits et al. [11] the influence of the overall carbon concentration to the mode of the phase transition is investigated. Simulations are done for a mixed-mode model, i. e. the lattice transformation and the carbon diffusion are included in the calculations. The character of the transformation is identified by evaluating the carbon concentration at the interface. The influence of mechanical effects, especially eigenstrains caused by the different densities of the two phases, is not considered there.

Dreyer and Duderstadt [3] present a model for phase transitions in gallium arsenide wafers, where effects due to mechanical stresses and strains are included. A similar approach is adopted in this work. The model presented here is not restricted to steel. In fact, the basic ideas are applicable to a wide range of problems, for example the modelling of charging and discharging processes in lithium batteries [4]. Similar to the case of steel, a sublattice model is used there to describe the constitution of the phases. In a work by Böhme et al. [1], a thermodynamical model for a general mixture of multiple components is given, where the mechanical displacement field is included. The model is derived in a systematical framework, taking into account the conservation laws for mass, momentum and energy as well as the second law of thermodynamics.

We describe the derivation of a sharp interface model, based on the afore mentioned physical principles. We concentrate on the modelling of one austenite grain as a typical part of the microstructure and neglect effects like grain coarsening or grain boundary diffusion. We restrict ourselves to the isothermal case, since on the scale of one iron grain heat conductivity is supposed to be fast compared to the diffusion of carbon and the migration of the interface. By means of numerical simulations for the interface-controlled case the influence of the misfit strains on the kinetics of the phase transformation is investigated.

The paper is organised as follows: in Section 2, the thermodynamical model based on the conservation laws for mass and momentum is described. We derive constitutive functions that are in accordance with the second law of thermodynamics. The mechanical displacement field is investigated in Section 3. Since the free energy is important for the description of phase transitions, Section 4 is devoted to the determination of this quantity. The underlying idea is a decomposition into a chemical part and a mechanical part, which accounts for the effects of the misfit strains. In Section 5, a special case is treated, i. e. we consider a spherical-symmetric iron grain and assume an interface-controlled transformation behaviour. In doing so, a system of equations is derived to compute the temporal evolution of the homogeneous carbon concentrations in austenite and ferrite. The section is concluded with the presentation of numerical results.

2 Thermodynamic description of the Fe-C system

In this section, we derive the thermodynamical model that describes the phase transition from austenite to ferrite in steel. Throughout this paper an upper index is used for denoting vectors. Furthermore, we make use of the sum convention, i. e. one has to sum if superscripts occur twice.

We consider a domain $\Omega := \Omega_\alpha \cup \Omega_\gamma \subset \mathbb{R}^3$, which is occupied by the two phases ferrite and austenite, denoted by the open domains Ω_α and Ω_γ, respectively, with $\Omega_\alpha \cap \Omega_\gamma = \emptyset$. The phases are separated by an interface $I := \overline{\Omega}_\alpha \cap \overline{\Omega}_\gamma$. The state of the system at a given absolute temperature T is described by the following variables

$$\begin{aligned} &n_a(t, x^j), \quad a \in \{\mathrm{Fe}, \mathrm{C}, \mathrm{V}\}, && \text{the mole densities of iron, carbon} \\ & && \text{and vacancies,} \\ &u^i(t, x^j) && \text{the displacement field,} \end{aligned} \tag{1}$$

which can depend on time t and position $x = (x^1, x^2, x^3) \in \Omega$.

2.1 The balances of the partial mole densities

The model is based on the following conservation laws of the partial mole densities

$$\frac{\partial n_{\mathrm{Fe}}}{\partial t} + \frac{\partial n_{\mathrm{Fe}} v^k_{\mathrm{Fe}}}{\partial x^k} = 0, \quad \frac{\partial n_{\mathrm{C}}}{\partial t} + \frac{\partial n_{\mathrm{C}} v^k_{\mathrm{C}}}{\partial x^k} = 0 \quad \text{and} \quad \frac{\partial n_{\mathrm{V}}}{\partial t} + \frac{\partial n_{\mathrm{V}} v^k_{\mathrm{V}}}{\partial x^k} = 0, \tag{2}$$

where v^k_a, $a \in \{\mathrm{Fe}, \mathrm{C}, \mathrm{V}\}$, are the partial velocities of iron, carbon and vacancies. Due to the sublattice model there is a restriction on the three mole densities. In austenite the number of host and sublattice sites is equal, that is $n_{\mathrm{Fe}} = n_{\mathrm{C}} + n_{\mathrm{V}}$, whereas in ferrite the number of sublattice sites is three times the number of host lattice sites: $3n_{\mathrm{Fe}} = n_{\mathrm{C}} + n_{\mathrm{V}}$. This side condition can be written as

$$\eta\, n_{\mathrm{Fe}} = n_{\mathrm{C}} + n_{\mathrm{V}} \qquad \text{with} \qquad \eta = \begin{cases} 3 & \text{in } \Omega_\alpha \\ 1 & \text{in } \Omega_\gamma, \end{cases} \tag{3}$$

where η is called the site ratio. The three mole densities are not independent and therefore one of the balance laws (2) must be the consequence of the two others. To guarantee this we define

$$\eta\, n_{\mathrm{Fe}} v^k_{\mathrm{Fe}} = n_{\mathrm{C}} v^k_{\mathrm{C}} + n_{\mathrm{V}} v^k_{\mathrm{V}} \tag{4}$$

and in the following we can restrict ourselves to the balances $(2)_1$ and $(2)_2$. To describe the state of the system, the mass density ρ and the barycentric velocity v^k of the mixture need to be defined. These quantities are given by

$$\rho = \rho_{\mathrm{Fe}} + \rho_{\mathrm{C}} \qquad \text{and} \qquad \rho v^k = \rho_{\mathrm{Fe}} v^k_{\mathrm{Fe}} + \rho_{\mathrm{C}} v^k_{\mathrm{C}}, \tag{5}$$

where $\rho_{\mathrm{Fe}} := m_{\mathrm{Fe}} n_{\mathrm{Fe}}$ and $\rho_{\mathrm{C}} := m_{\mathrm{C}} n_{\mathrm{C}}$ are the partial mass densities of iron and carbon, m_{Fe} and m_{C} denote the corresponding molecular weights. Since vacancies have no mass, they do not contribute to the mass density and the barycentric velocity.

Next, the diffusion fluxes with respect to v^k are defined for each constituent

$$j^k_{\mathrm{Fe}} := n_{\mathrm{Fe}}(v^k_{\mathrm{Fe}} - v^k), \quad j^k_{\mathrm{C}} := n_{\mathrm{C}}(v^k_{\mathrm{C}} - v^k) \quad \text{and} \quad j^k_{\mathrm{V}} := n_{\mathrm{V}}(v^k_{\mathrm{V}} - v^k). \tag{6}$$

Expressions (4) and (5) lead to the identities

$$\eta j^k_{\mathrm{Fe}} = j^k_{\mathrm{C}} + j^k_{\mathrm{V}} \qquad \text{and} \qquad m_{\mathrm{Fe}} j^k_{\mathrm{Fe}} + m_{\mathrm{C}} j^k_{\mathrm{C}} = 0. \tag{7}$$

These relations can be used to eliminate j^k_{Fe} and j^k_{V}, such that only the diffusion flux of carbon has to be considered. In the following this flux is denoted by $j^k := j^k_{\mathrm{C}}$. Introducing the diffusion fluxes into the balance equations (2) one obtains together with $(7)_2$ the following partial differential equations

$$\left.\begin{aligned} \frac{\partial n_{\mathrm{Fe}}}{\partial t} + \frac{\partial n_{\mathrm{Fe}} v^k}{\partial x^k} - \frac{m_{\mathrm{C}}}{m_{\mathrm{Fe}}} \frac{\partial j^k}{\partial x^k} &= 0 \\ \frac{\partial n_{\mathrm{C}}}{\partial t} + \frac{\partial n_{\mathrm{C}} v^k}{\partial x^k} + \frac{\partial j^k}{\partial x^k} &= 0 \end{aligned}\right\} \quad \text{in } \Omega. \tag{8}$$

This is a system of diffusion equations for the mole densities of iron and carbon. The diffusion flux j^k is related to the variables introduced in (1) by a general version of Fick's law

$$j^k = -M^B \frac{\partial}{\partial x^k} \left(\mu - \frac{\eta m_{\mathrm{C}}}{m_{\mathrm{Fe}}} \mu_{\mathrm{V}} \right) \tag{9}$$

with $\mu := \mu_{\mathrm{C}} - \mu_{\mathrm{V}}$ and $M^B > 0$ denoting the mobility of the carbon atoms. The quantities μ_{C} and μ_{V} represent the chemical potentials of carbon and vacancies, which can be expressed in dependence on the mole densities and the mechanical displacement. For a detailed derivation of the relation (9), by evaluating the second law of thermodynamics, we refer to Appendix A.1. The chemical potentials will be introduced in Section 4.

On the outer boundary $\partial\Omega$ with the outward unit normal vector ν^k, Neumann boundary conditions are imposed on the diffusion flux

$$j^k \nu^k = 0 \qquad \text{on } \partial\Omega.$$

On the interface I the mole densities are discontinuous. These discontinuities can be expressed by jump conditions. Similar to the conservation laws (2) in the bulk, one can define conservation laws on I. The material mole flux across the interface is conserved, which can be written as

$$[[n_{\mathrm{Fe}} v^{\nu}_{\mathrm{Fe}}]] - [[n_{\mathrm{Fe}}]] w^{\nu} = 0 \qquad \text{and} \qquad [[n_{\mathrm{C}} v^{\nu}_{\mathrm{C}}]] - [[n_{\mathrm{C}}]] w^{\nu} = 0 \quad \text{on } I, \tag{10}$$

where ν^k and $w^\nu := w^i \nu^i$ denote the unit normal vector pointing from Ω_γ to Ω_α and the normal interfacial velocity. The double bracket indicates the jump of a quantity across the interface: $[[\psi]] = \psi^\alpha - \psi^\gamma$. As an abbreviation the interfacial mole fluxes are defined as

$$\dot{\mathcal{N}}_{\mathrm{Fe}} := n_{\mathrm{Fe}}(v^{\nu}_{\mathrm{Fe}} - w^{\nu}) \qquad \text{and} \qquad \dot{\mathcal{N}}_{\mathrm{C}} := n_{\mathrm{C}}(v^{\nu}_{\mathrm{C}} - w^{\nu}). \tag{11}$$

We conclude by (10) that they are continuous across the interface

$$\dot{\mathcal{N}}^{\alpha}_{\mathrm{Fe}} = \dot{\mathcal{N}}^{\gamma}_{\mathrm{Fe}} \qquad \text{and} \qquad \dot{\mathcal{N}}^{\alpha}_{\mathrm{C}} = \dot{\mathcal{N}}^{\gamma}_{\mathrm{C}} \qquad \text{on } I. \tag{12}$$

In analogy to the constitutive function (9) for the diffusion flux j^k one can derive the following relations for the interfacial mole fluxes defined in (11)

$$\dot{\mathcal{N}}_{\mathrm{Fe}} = -M^{I}_{\mathrm{Fe}}[[\eta \mu_{\mathrm{V}} - \frac{m_{\mathrm{Fe}}}{\rho} \sigma^{\langle ij \rangle} \nu^i \nu^j]] \quad \text{and} \quad \dot{\mathcal{N}}_{\mathrm{C}} = -M^{I}_{\mathrm{C}}[[\mu - \frac{m_{\mathrm{C}}}{\rho} \sigma^{\langle ij \rangle} \nu^i \nu^j]]. \tag{13}$$

The quantities $M^I_{\mathrm{Fe}} > 0$ and $M^I_{\mathrm{C}} > 0$ are the interface mobilities of iron and carbon. The newly introduced expression $\sigma^{\langle ij \rangle}$ denotes the trace-free or deviatoric part of the Cauchy stress tensor σ^{ij}, see Section 2.2, which is obtained by the decomposition $\sigma^{ij} = \frac{1}{3}\sigma^{kk}\delta^{ij} + \sigma^{\langle ij \rangle}$. The kinematic conditions (13) specify the interface migration in terms of the interface velocity w^ν. They can be derived by evaluating the second law of thermodynamics on the interface, see Appendix A.2.

Instead of the mole density n_{C}, the carbon content is often expressed in terms of the site fraction of carbon, y, defined as the ratio of sublattice sites occupied by carbon and overall density of sublattice sites, i. e.

$$y := \frac{n_{\mathrm{C}}}{n_{\mathrm{C}} + n_{\mathrm{V}}} = \frac{n_{\mathrm{C}}}{\eta n_{\mathrm{Fe}}}. \tag{14}$$

2.2 The quasistatic balance of momentum

In order to determine the deformation of the iron lattice in terms of the displacement field u^i, the balance of momentum is examined. Since mechanical equilibrium is attained much faster than chemical equilibrium, one can consider the quasistatic case, which reads

$$\frac{\partial \sigma^{ij}}{\partial x^j} = 0 \qquad \text{in } \Omega. \tag{15}$$

The quantity σ^{ij} denotes the Cauchy stress tensor, which is related to the displacement field u^i by a constitutive law. A detailed description of the stress, strain and the displacement, including the constitutive relation, is given in the next section.

As boundary conditions we impose

$$\sigma^{ij}\nu^j = -p_0\nu^i \qquad \text{on } \partial\Omega, \tag{16}$$

where p_0 is a constant outer pressure. This boundary condition refers to the pressure-controlled case. Due to the fact that the pressure is fixed, the volume of the body can change. Another possibility is the volume-controlled case, where a prescribed volume V_0 of the body is considered, i. e. one would impose Dirichlet boundary conditions on the displacement u^i.

The interfacial condition for σ^{ij} is the following

$$[[\sigma^{ij}]]\nu^j = -2\gamma k_M\nu^i \qquad \text{on } I. \tag{17}$$

The quantities $\gamma > 0$ and k_M denote the isotropic surface tension and the mean curvature of the interface. For the derivation of this jump condition see e. g. [2].

3 Description of the motion, stress and strain

In this section we describe the deformation of a body and we relate the displacement field to the stresses and strains. For that purpose, a reference state is introduced, where the body occupies the domain Ω^R. The position of a material point in the reference state is given by the coordinates $X = (X^1, X^2, X^3) \in \Omega^R$. At time t the body is deformed and covers the domain $\Omega(t)$. The position of a point in this configuration is given by the coordinates $x \in \Omega(t)$. There exists a bijective mapping

$$x^i = \chi^i(t, X^j), \tag{18}$$

which maps Ω^R onto $\Omega(t)$. This mapping is called motion or deformation. With the help of this function, the displacement field $\hat{u}^i$ and the barycentric velocity $\hat{v}^i$ are defined as

$$\hat{u}^i(t, X^j) := \chi^i(t, X^j) - X^i \quad \text{and} \quad \hat{v}^i(t, X^j) := \frac{\partial\chi^i(t, X^j)}{\partial t} = \frac{\partial\hat{u}^i(t, X^j)}{\partial t}. \tag{19}$$

Furthermore, we introduce the displacement gradient and the deformation gradient

$$H^{ij} := \frac{\partial\hat{u}^i}{\partial X^j} \qquad \text{and} \qquad F^{ij} := \frac{\partial\chi^i}{\partial X^j} \quad \text{with} \quad J := \det F^{ij} > 0. \tag{20}$$

The quantities above are expressed with respect to the reference configuration. This description is called the Lagrangian or material description. The positivity of J guarantees invertibility of $\chi^i(t, X^j)$ and one can write

$$X^i = (\chi^{-1})^i(t, x^j). \tag{21}$$

The inverse of the motion is used to give a representation of the displacement and the barycentric velocity with respect to the configuration at time t, which is known as the Eulerian or spatial description,

$$u^i(t, x^j) := \hat{u}^i(t, \chi^{-1}(t, x^j)) \qquad \text{and} \qquad v^i(t, x^j) := \hat{v}^i(t, \chi^{-1}(t, x^j)). \tag{22}$$

Analogously to (20) one defines the displacement- and deformation gradient in Eulerian coordinates as

$$h^{ij} := \frac{\partial u^i}{\partial x^j} \qquad \text{and} \qquad (F^{-1})^{ij} := \frac{\partial (\chi^{-1})^i}{\partial x^j}. \tag{23}$$

Measures for the strains caused by the deformation are e. g. the right Cauchy-Green tensor C^{ij} and its unimodular part c^{ij}, defined as

$$C^{ij} := F^{ki} F^{kj} \qquad \text{and} \qquad c^{ij} := J^{-\frac{2}{3}} C^{ij}. \tag{24}$$

Note that there holds $\det(c^{ij}) = 1$, thus, C^{ij} is split into a part $J^{-2/3}$, which describes pure changes of the volume, whereas c^{ij} indicates changes of the shape of a body.

To describe the stress-strain relation, we take into consideration that deformations of the iron lattice result from two independent effects. The first one are inelastic deformations, which are caused by changes of the volume due to variations of the carbon fraction y and the lower density of the developing ferrite phase. The second effect are elastic deformations caused for example by external loadings.

One can account for these effects by introducing three states that are characterised by y and F^{ij}, compare also to Böhme et al. [1]. The first one is an undeformed reference state $\overline{S}$ at reference pressure $\overline{p}$ with the coordinates (X^1, X^2, X^3). It consists of a single phase and is characterised by the carbon fraction $\overline{y} = 0$ and the deformation gradient $\overline{F}^{ij} = \delta^{ij}$.

The second state, denoted by S^* with the coordinates (X_*^1, X_*^2, X_*^3), is reached from the reference state at constant reference pressure $\overline{p}$ by raising the carbon fraction to $y^* = y$. Furthermore, we allow for a massive phase transition in this state. The corresponding deformation gradient is given by F_*^{ij}. The transition from $\overline{S}$ to S^* describes the inelastic deformation.

The third state S is the actual state with the coordinates (x^1, x^2, x^3) and the deformation gradient F^{ij} (with respect to the reference configuration). It is reached from the state S^* by a purely elastic deformation F_e^{ij} with no further change in y.

For the states $\overline{S}, S^*$ and S we introduce the iron mole densities $\overline{n}_{\mathrm{Fe}}, n_{\mathrm{Fe}}^*$ and n_{Fe}, the mass densities

$$\overline{\rho} = m_{\mathrm{Fe}} \overline{n}_{\mathrm{Fe}}, \qquad \rho^* = m(y) n_{\mathrm{Fe}}^* \qquad \text{and} \qquad \rho = m(y) n_{\mathrm{Fe}}, \tag{25}$$

where $m(y) = m_{\mathrm{Fe}} + m_{\mathrm{C}} \eta y$ denotes the mean molecular weight, and the determinants

$$J_* = \det(F_*^{ij}) = \frac{\overline{\rho}}{\rho^*}, \quad J = \det(F^{ij}) = \frac{\overline{\rho}}{\rho} \quad \text{and} \quad J_e = \det(F_e^{ij}) = \frac{\rho^*}{\rho}. \tag{26}$$

For the deformation gradients holds $F^{ij} = F_e^{ik} F_*^{kj}$. This is a consequence of the chain rule applied to

$$x^i = \chi^i(t, X^j) = \chi_e^i(t, \chi_*^k(t, X^j)). \tag{27}$$

The deformation gradient $\underset{*}{F}^{ij}$ for the state S^* is established as follows. The reference state $\overline{S}$ is known. The deformation from the state $\overline{S}$ to S^* is a pure change of the volume. Therefore, it holds

$$\frac{\overline{n}_{\mathrm{Fe}}}{n^*_{\mathrm{Fe}}} = \frac{V_*(y)}{\overline{V}}, \tag{28}$$

where $\overline{V}$ is the volume of the reference state and $V_*(y)$ is the volume of the body at the state S^*. This volume is obtained by measurements of the lattice constant in dependence on the carbon fraction y, see for example [9]. With (25), (26) and a linear interpolation of the data given in [9] there results

$$\underset{*}{F}^{ij} = J_*(y)^{\frac{1}{3}}\delta^{ij} \quad \text{with} \quad J_*(y) = \frac{m_{\mathrm{Fe}}}{m(y)}\frac{V^\ell_m}{\overline{V}}(1+\delta^\ell y) \quad \text{in } \Omega_\ell, \quad \ell = \alpha, \gamma, \tag{29}$$

where V^ℓ_m and $\delta^\ell, \ell = \alpha, \gamma$, denote the molar volume and the linear expansion coefficient for the respective phase.

The constitutive equation relating the stress to the strain is given in terms of the St. Venant-Kirchhoff law, which is formulated for the second Piola-Kirchhoff stress tensor. We denote this tensor with respect to the state $\overline{S}$ by t^{ij} and with respect to the state S^* by z^{ij} . The Cauchy stress tensor σ^{ij} is the same for both descriptions and it holds

$$\sigma^{ij} = J^{-1}F^{ik}F^{jl}t^{kl} \qquad \text{and} \qquad \sigma^{ij} = \underset{e}{J}^{-1}\underset{e}{F}^{ik}\underset{e}{F}^{jl}z^{kl}. \tag{30}$$

Elimination of σ^{ij} together with $F^{ij} = \underset{e}{F}^{ik}\underset{*}{F}^{kj}$ leads to

$$t^{ij} = J_*\underset{*}{F}^{-ik}\underset{*}{F}^{-jl}z^{kl}. \tag{31}$$

Now, the constitutive relation is formulated in terms of the St. Venant-Kirchhoff law for z^{ij} as a purely elastic deformation

$$z^{ij} = -\overline{p}J_e\underset{e}{C}^{-ij} + \frac{1}{2}\tilde{K}^{ijkl}(\underset{e}{C}^{kl} - \delta^{kl}). \tag{32}$$

The tensor $\tilde{K}^{ijkl}$ denotes the stiffness tensor. The data for α- and γ-iron are given e. g. by Inal et al. [8]. There is only a small difference in the elastic coefficients given in literature for different kinds of steel (with different carbon content) and pure iron. Therefore, we assume that $\tilde{K}^{ijkl}$ is independent of the carbon fraction y.

To calculate the chemical potentials, as it is described in Section 4, a formulation for t^{ij} is necessary. Applying the transformation rule (31), we obtain the following constitutive law for the 2nd Piola-Kirchhoff tensor

$$t^{ij} = -\overline{p}JC^{-ij} + \frac{1}{2}K^{ijkl}(y)(C^{kl} - \underset{*}{C}^{kl}(y)), \tag{33}$$

where

$$K^{ijkl}(y) := J_*\underset{*}{F}^{-im}\underset{*}{F}^{-jn}\underset{*}{F}^{-ko}\underset{*}{F}^{-lp}\tilde{K}^{mnop} = J_*(y)^{-\frac{1}{3}}\tilde{K}^{ijkl} \tag{34}$$

is a modified stiffness tensor and $\underset{*}{C}^{kl} = \underset{*}{F}^{mk}\underset{*}{F}^{ml}$ describes the misfit strain.

4 Determination of the free energy

In order to study the γ/α-phase transition in steel, knowledge of the free energy density $\rho\psi$ is necessary to obtain explicit expressions for the chemical potentials. The determination of these quantities is the subject of this section. For that purpose, we assume that the function ψ has the following representations

$$\psi = \psi(T, n_{\mathrm{C}}, n_{\mathrm{V}}, c^{ij}) = \hat{\psi}(T, y, \rho, c^{ij}) = \tilde{\psi}(T, y, C^{ij}). \tag{35}$$

The different functions represent the dependence of the free energy on different sets of variables, which can be converted by the relations (5), (14), (24) and (26). The strategy to determine ψ is the following. Starting from the equation

$$t^{ij} = 2\overline{\rho}\frac{\partial\tilde{\psi}}{\partial C^{ij}}, \tag{36}$$

which is a consequence of the second law of thermodynamics, see Appendix A.1 or [1], we determine the function $\tilde{\psi}(T, y, C^{ij})$ by integration of (33). This yields

$$\tilde{\psi}(T, y, C^{ij}) = -\frac{\overline{p}}{\overline{\rho}}J + \frac{1}{8\overline{\rho}}\left(C^{ij} - C_*^{ij}(y)\right)K^{ijkl}\left(C^{kl} - C_*^{kl}(y)\right) + \mathcal{K}(T, y), \tag{37}$$

where $\mathcal{K}(T, y)$ is an integration constant. This constant is obtained by a decomposition of the free energy into a mechanical part $\tilde{\psi}^{\mathrm{mech}}(T, y, C^{ij})$ and a chemical part $\tilde{\psi}^{\mathrm{chem}}(T, y)$, which does not depend on the deformation of the body, see also [3],

$$\tilde{\psi}(T, y, C^{ij}) = \tilde{\psi}^{\mathrm{chem}}(T, y) + \tilde{\psi}^{\mathrm{mech}}(T, y, C^{ij}). \tag{38}$$

Such a decomposition is motivated by the fact that the chemical and the mechanical part of the free energy are determined in different ways. The computation of the mechanical part is based on a constitutive relation, whereas the chemical part is obtained by thermodynamical measurements.

We define that at the state S^* the mechanical part of the free energy $\tilde{\psi}^{\mathrm{mech}}(T, y, C_*^{ij})$ vanishes, so that $\tilde{\psi}(T, y, C_*^{ij}) = \tilde{\psi}^{\mathrm{chem}}(T, y)$. Hence, the integration constant is given by $\mathcal{K}(T, y) = \tilde{\psi}^{\mathrm{chem}}(T, y) + J_*(y)\overline{p}/\overline{\rho}$ and one obtains

$$\rho\tilde{\psi}^{\mathrm{mech}}(T, y, C^{ij}) = \overline{p}\left(\frac{J_*}{J} - 1\right) + \frac{1}{8J}\left(C^{ij} - C_*^{ij}(y)\right)K^{ijkl}(y)\left(C^{kl} - C_*^{kl}(y)\right) \tag{39}$$

with $J = \det(F^{ij}) = \det(C^{ij})^{1/2}$.

The determination of the chemical part of the free energy is based on thermodynamical measurements. The evaluation of the iron-carbon system can be found for example in [6] or [10]. There, $\rho\psi^{\mathrm{chem}}$ is given as

$$\begin{aligned}\rho\psi^{\mathrm{chem}}(T, n_{\mathrm{C}}, n_{\mathrm{V}}) = n_{\mathrm{Fe}}\Big[&G_{\mathrm{FeC}}(T)y + G_{\mathrm{FeV}}(T)(1-y) - L(T)y(1-y)\\ &+ \eta RT(y\ln y + (1-y)\ln(1-y)) + G_m^{\alpha}(T)\Big] =: n_{\mathrm{Fe}}f(y)\end{aligned} \tag{40}$$

with R denoting the universal gas constant. The quantities n_{Fe} and y are related to n_{C} and n_{V} by (3) and (14). The coefficients $G_{\mathrm{FeC}}, G_{\mathrm{FeV}}$ and L are temperature dependent functions. The part G_m^α is a magnetic contribution which only occurs in the α-phase. These parameters are taken from [6]. The function f is introduced as an abbreviation for the term in brackets, which only depends on y when the temperature T is fixed.

Now, we can calculate the chemical potentials, defined as

$$\mu_{\mathrm{C}} := \frac{\partial \rho\psi(T, n_{\mathrm{C}}, n_{\mathrm{V}}, c^{ij})}{\partial n_{\mathrm{C}}} \qquad \text{and} \qquad \mu_{\mathrm{V}} := \frac{\partial \rho\psi(T, n_{\mathrm{C}}, n_{\mathrm{V}}, c^{ij})}{\partial n_{\mathrm{V}}}. \tag{41}$$

Carrying (38), (39) and (40) into (41) one finally obtains

$$\begin{aligned} \mu_{\mathrm{C}} = {} & \frac{1}{\eta}(f(y) + (1-y)f'(y)) \\ & + \frac{1}{\eta\bar{\rho}}\bigg[(\eta m_{\mathrm{C}} + m_{\mathrm{Fe}}) \Big(\overline{p} J_*(y) - \frac{1}{8}(\frac{1}{3}C^{ij} + C_*^{ij}(y))K^{ijkl}(y)(C^{kl} - C_*^{kl}(y)) \Big) \\ & \quad + (1-y)m(y) \Big(\overline{p} J_*'(y) + \frac{1}{8}(C^{ij} - C_*^{ij}(y))(K')^{ijkl}(y)(C^{kl} - C_*^{kl}(y)) \\ & \qquad - \frac{1}{4}(C_*')^{ij}(y)K^{ijkl}(y)(C^{kl} - C_*^{kl}(y)) \Big) \bigg] \end{aligned} \tag{42}$$

and for the chemical potential of the vacancies

$$\begin{aligned} \mu_{\mathrm{V}} = {} & \frac{1}{\eta}(f(y) - yf'(y)) \\ & + \frac{1}{\eta\bar{\rho}}\bigg[m_{\mathrm{Fe}} \Big(\overline{p} J_*(y) - \frac{1}{8}(\frac{1}{3}C^{ij} + C_*^{ij}(y))K^{ijkl}(y)(C^{kl} - C_*^{kl}(y)) \Big) \\ & \quad - y\, m(y) \Big(\overline{p} J_*'(y) + \frac{1}{8}(C^{ij} - C_*^{ij}(y))(K')^{ijkl}(y)(C^{kl} - C_*^{kl}(y)) \\ & \qquad - \frac{1}{4}(C_*')^{ij}(y)K^{ijkl}(y)(C^{kl} - C_*^{kl}(y)) \Big) \bigg], \end{aligned} \tag{43}$$

where the prime denotes differentiation with respect to the site fraction y.

5 A simplified model with spherical symmetry

Performing numerical simulations for the presented free boundary problem is quite complex. It involves suitable algorithms to calculate the position of the free boundary. In order to obtain numerical results for the simulation of the austenite-ferrite phase transition, we make some assumptions to get a simplified model. First of all, we consider a spherical-symmetric geometry. The iron grain is modelled as a sphere with radius r_0. The γ-phase forms the inner core with time dependent radius r_I

and the α-phase is an outer shell, i. e. $\Omega_\gamma = (0, r_I)$ and $\Omega_\alpha = (r_I, r_0)$. This is motivated by the fact that ferrite usually nucleates at grain boundaries and grows into the austenite matrix. The radius r_0 is time dependent, too. The two phases have different densities and due to the fixed outer pressure the overall volume changes.

Furthermore, we restrict ourselves to the interface-controlled case, i. e. the bulk mobility of carbon M^B is infinitely large compared to the interface mobilities M^I_{Fe} and M^I_{C}. Since the diffusion flux must be finite, we get from equation (9) that the gradient of the chemical potentials must be equal to zero and therefore the mole densities n_{Fe} and n_{C} are homogeneous in regular points. For a low mean carbon concentration this is a well accepted assumption. If the overall carbon concentration is higher, a diffusion-controlled transformation behaviour, where the diffusion of carbon in the bulk becomes the rate determining process, is a more realistic description, see e. g. [11]. Nevertheless, we consider the interface-controlled case in this study.

Concerning the mechanical equations we make the following simplifications. To be in accordance with the spherical symmetry, we neglect the cubical anisotropy of the iron lattice and consider an isotropic stiffness tensor with Lamé constants λ and μ, which are obtained from the coefficients given in [8] by taking an average. Moreover, we assume that the deformations are small so that we can replace the constitutive law (33), relating the stress tensor to the displacement, by its linearisation in the displacement gradient h^{ij}.

The variables for this simplified interface-controlled model are the homogeneous carbon fractions and iron mole densities $y^\alpha, y^\gamma, n^\alpha_{\mathrm{Fe}}$ and n^γ_{Fe}, which do not depend on the space variable r, but differ in the two phases, and the radii r_I and r_0. In the following a set of equations to compute the temporal evolution of these variables is derived and numerical results are presented.

5.1 The balances of the mole densities

The balance laws for the mole densities in the spherical-symmetric case are the following

$$\frac{\partial n_{\mathrm{Fe}}}{\partial t} + \frac{1}{r^2}\frac{\partial r^2 n_{\mathrm{Fe}} v_{\mathrm{Fe}}}{\partial r} = 0 \qquad \text{and} \qquad \frac{\partial n_{\mathrm{C}}}{\partial t} + \frac{1}{r^2}\frac{\partial r^2 n_{\mathrm{C}} v_{\mathrm{C}}}{\partial r} = 0. \tag{44}$$

On the interface I, which is given by the radius r_I, we have by (10)

$$n^\alpha_{\mathrm{Fe}}(v^\alpha_{\mathrm{Fe}} - \dot{r}_I) = n^\gamma_{\mathrm{Fe}}(v^\gamma_{\mathrm{Fe}} - \dot{r}_I) \qquad \text{and} \qquad n^\alpha_{\mathrm{C}}(v^\alpha_{\mathrm{C}} - \dot{r}_I) = n^\gamma_{\mathrm{C}}(v^\gamma_{\mathrm{C}} - \dot{r}_I). \tag{45}$$

Derivatives with respect to time t are denoted by a dot. The boundary conditions for the partial velocities of iron and carbon are

$$\lim_{r\to 0} r^2 v_a = 0 \qquad \text{and} \qquad v_a = \dot{r}_0 \quad \text{at } r = r_0, \quad a \in \{\mathrm{Fe}, \mathrm{C}\}. \tag{46}$$

Since the mole densities are homogeneous in Ω_α and Ω_γ, the partial velocities can be explicitly determined using the conservation laws (44). One obtains for the domain

Ω_γ by applying the boundary condition $(46)_1$ for both constituents

$$v_a^\gamma = -\frac{\dot{n}_a^\gamma}{3n_a^\gamma} r, \qquad a \in \{\mathrm{Fe}, \mathrm{C}\}, \tag{47}$$

whereas in Ω_α we have with $(46)_2$

$$v_a^\alpha = -\frac{\dot{n}_a^\alpha}{3n_a^\alpha} \frac{r^3 - r_0^3}{r^2} + \dot{r}_0 \frac{r_0^2}{r^2}, \qquad a \in \{\mathrm{Fe}, \mathrm{C}\}. \tag{48}$$

In the homogeneous case the jump conditions (45) together with the equations for the partial velocities can be integrated with respect to time. One obtains global conservation laws for the mole densities of iron and carbon

$$n_{\mathrm{Fe}}^\gamma r_I^3 + n_{\mathrm{Fe}}^\alpha (r_0^3 - r_I^3) = c_1 \quad \text{and} \quad y^\gamma n_{\mathrm{Fe}}^\gamma r_I^3 + 3y^\alpha n_{\mathrm{Fe}}^\alpha (r_0^3 - r_I^3) = c_2, \tag{49}$$

where the site fractions y, defined in (14), are used instead of n_{C}. The constants c_1 and c_2 can be determined by the initial data at time t_0. Under consideration of $(49)_1$, equation $(49)_2$ can be simplified as follows

$$(y^\gamma - 3y^\alpha) n_{\mathrm{Fe}}^\gamma r_I^3 + 3y^\alpha c_1 = c_2. \tag{50}$$

Regarding the kinematic conditions (13), a further simplification is introduced. We assume that the motion of the interface is only determined by the transformation of the iron lattice from the fcc to the bcc structure. The rearrangement of carbon atoms at the interface is supposed to occur instantaneously, i. e. $M_{\mathrm{C}}^I \gg M_{\mathrm{Fe}}^I$. Thus, we set $M_{\mathrm{C}}^I = \infty$. Since the flux of carbon atoms through the interface $\dot{\mathcal{N}}_{\mathrm{C}}$ is finite, the second factor in $(13)_2$ must be zero. The kinematic conditions reduce to

$$\frac{1}{3}\dot{n}_{\mathrm{Fe}}^\gamma r_I + n_{\mathrm{Fe}}^\gamma \dot{r}_I = M_{\mathrm{Fe}}^I [[\eta \mu_{\mathrm{V}} - \frac{m_{\mathrm{Fe}}}{\rho} \sigma^{\langle rr \rangle}]] \qquad \text{and} \qquad [[\mu - \frac{m_{\mathrm{C}}}{\rho} \sigma^{\langle rr \rangle}]] = 0, \tag{51}$$

i. e. the chemical potential μ is always in equilibrium and the interface migration is solely determined by $(51)_1$.

Since there is no diffusion of iron atoms, the mole density n_{Fe} is directly related to the mechanical displacement field. The computation of the displacement for the simplified model is considered in the next section.

5.2 The linearised mechanical subproblem in spherical coordinates

Before we analyse the balance of momentum in spherical coordinates, the stress-strain relation is linearised with respect to the displacement gradient h^{ij}. It is assumed that the deformations are small such that higher order terms in the displacement gradient can be neglected. By equations (19), (22) and (23) there holds

$$(F^{-1})^{ij} = \delta^{ij} - h^{ij} \qquad \text{and} \qquad (C^{-1})^{ij} = \delta^{ij} - h^{ij} - h^{ji} + h^{ki}h^{kj}. \tag{52}$$

The inverse matrices up to linear order are given by

$$F^{ij} = \delta^{ij} + h^{ij} + \mathcal{O}(\|h^{ij}\|^2) \qquad \text{and} \qquad C^{ij} = \delta^{ij} + h^{ij} + h^{ji} + \mathcal{O}(\|h^{ij}\|^2). \tag{53}$$

For the Jacobian we have $J^{-1} = 1 - h^{kk} + \mathcal{O}(\|h^{ij}\|^2)$. Furthermore, for the intermediate state S^* a function $h^*(y)$, which is supposed to be of the same order as the deformation gradient, is introduced such that

$$(F_*^{-1})^{ij} = (1 - h^*)\delta^{ij} \qquad \text{and} \qquad J_*^{-1} = (1 - h^*)^3. \tag{54}$$

Now we obtain from

$$\sigma^{ij} = J^{-1} F^{im} F^{jn} t^{mn} \quad \text{and} \quad t^{ij} = -\overline{p} J (C^{-1})^{ij} + \frac{1}{2} K^{ijkl} (C^{kl} - C_*^{kl}) \tag{55}$$

the following representation for the stress tensor within the linear order of approximation

$$\sigma^{ij} = -\overline{p} + \frac{1}{2} \tilde{K}^{ijkl} (h^{kl} + h^{lk} - 2h^* \delta^{kl}). \tag{56}$$

This can be interpreted in the sense of the classical Hooke law with a misfit strain, represented by $h^*(y)$. Neglecting the cubical anisotropy of the iron lattice, the stiffness tensor $\tilde{K}^{ijkl}$ is given by

$$\tilde{K}^{ijkl} = \lambda \delta^{ij} \delta^{kl} + \mu (\delta^{ik} \delta^{jl} + \delta^{il} \delta^{jk}), \tag{57}$$

where λ and μ are the Lamé constants. Then, the stress tensor can be written as

$$\sigma^{ij} = -\overline{p} + \lambda h^{kk} \delta^{ij} + \mu (h^{ij} + h^{ji}) - (3\lambda + 2\mu) h^* \delta^{ij}. \tag{58}$$

Now we rewrite the balance of momentum in spherical coordinates (r, ϕ, θ). Due to the assumed spherical symmetry, the displacement field can be simplified to $(u^r, u^\phi, u^\theta) = (u(r), 0, 0)$ and for the displacement gradient we have

$$h^{rr} = \frac{\partial u}{\partial r}, \quad h^{\phi\phi} = h^{\theta\theta} = \frac{u}{r} \quad \text{and} \quad h^{ij} = 0 \quad \text{otherwise}. \tag{59}$$

From (58) one obtains that $\sigma^{\phi\phi} = \sigma^{\theta\theta}$ and $\sigma^{r\phi} = \sigma^{r\theta} = \sigma^{\phi\theta} = 0$. The nonzero components of the stress tensor are

$$\begin{aligned} \sigma^{rr} &= -\overline{p} + \lambda (h^{rr} + 2h^{\phi\phi}) + 2\mu h^{rr} - (3\lambda + 2\mu) h^*, \\ \sigma^{\phi\phi} &= -\overline{p} + \lambda (h^{rr} + 2h^{\phi\phi}) + 2\mu h^{\phi\phi} - (3\lambda + 2\mu) h^*. \end{aligned} \tag{60}$$

The balance of momentum (15) reduces to the following equation, see e. g. [5],

$$\frac{\partial \sigma^{rr}}{\partial r} + 2 \frac{\sigma^{rr} - \sigma^{\phi\phi}}{r} = 0 \qquad \text{for } r \in \Omega \tag{61}$$

with the jump and boundary conditions

$$[[\sigma^{rr}(r_I)]] = -\frac{2\gamma}{r_I} \qquad \text{and} \qquad \sigma^{rr}(r_0) = -p_0. \tag{62}$$

Furthermore, we impose the following conditions on the displacement $u(r)$ (regularity at $r = 0$ and continuity at the interface)

$$\lim_{r\to 0} u(r) = 0 \qquad \text{and} \qquad [[u(r_I)]] = 0. \tag{63}$$

Inserting the representation for the stress tensor (60) into equation (61), one obtains with $h^{rr} = u'(r)$ and $h^{\theta\theta} = u(r)/r$ an ordinary differential equation for the displacement $u(r)$ that is given by

$$u'' + \frac{2}{r}\left(u' - \frac{u}{r}\right) = 0. \tag{64}$$

Note that due to the assumed homogeneity of the carbon fractions y^α and y^γ the function h^* does not depend on r. With the conditions (63) on $u(r)$, the solution to this ODE is the following

$$u(r) = \begin{cases} (a+b)r & \text{for } r \in [0, r_I) \\ ar + b\frac{r_I^3}{r^2} & \text{for } r \in [r_I, r_0]. \end{cases} \tag{65}$$

The constants a and b, which can depend on r_I, r_0 as well as on the homogeneous carbon fractions y^α and y^γ, are defined via the boundary conditions (62). One obtains explicitly

$$\begin{aligned} a &= \frac{\overline{p} - p_0}{3K_\alpha} + h^*_\alpha(y^\alpha) + \frac{4\mu_\alpha}{3K_\alpha}\frac{r_I^3}{r_0^3} b, \\ b &= c_0^{-1}\left(\frac{2\gamma}{r_I} - 3K_\gamma(h^*_\alpha(y^\alpha) - h^*_\gamma(y^\gamma)) + \kappa(\overline{p} - p_0)\right). \end{aligned} \tag{66}$$

As an abbreviation we introduced the bulk moduli $K_\ell = \lambda_\ell + 2/3\mu_\ell,\ \ell = \alpha, \gamma$, for the respective phases, $\kappa = 1 - K_\gamma/K_\alpha$ and $c_0 = 3K_\gamma + 4\mu_\alpha(1 - \kappa(r_I/r_0)^3)$.

Finally, we have an explicit representation for the displacement in dependence on y^α, y^γ, r_I and r_0. To relate the displacement to the mole density of iron, recall relation $(26)_2$. Within the linear order of approximation holds

$$J^{-1} = 1 - h^{kk}, \qquad \text{where} \qquad J^{-1} = \frac{\rho}{\overline{\rho}} = \frac{m(y) n_{\mathrm{Fe}}}{m_{\mathrm{Fe}} \overline{n}_{\mathrm{Fe}}}, \tag{67}$$

such that we obtain

$$\frac{n_{\mathrm{Fe}}}{\overline{n}_{\mathrm{Fe}}} = \frac{m_{\mathrm{Fe}}}{m(y)}(1 - h^{kk}). \tag{68}$$

The chemical potentials (41) and (42) can be written within the same order of approximation as

$$\begin{aligned} \mu_{\mathrm{C}} = \frac{1}{\eta}(f + (1-y)f') + \frac{1}{\eta\overline{\rho}}\Big[&(\eta m_{\mathrm{C}} + m_{\mathrm{Fe}})\left(\overline{p} J_* - K(h^{kk} - 3h^*)\right) \\ &+ (1-y)m(y)J_*'\left(\overline{p} - K(h^{kk} - 3h^*)\right)\Big] \end{aligned} \tag{69}$$

and

$$\mu_{\mathrm{V}} = \frac{1}{\eta}(f - yf') + \frac{1}{\eta\overline{\rho}}\Big[m_{\mathrm{Fe}}\left(\overline{p}J_* - K(h^{kk} - 3h^*)\right) \\ - y\,m(y)J_*'\left(\overline{p} - K(h^{kk} - 3h^*)\right)\Big]. \quad (70)$$

For the spherical symmetric problem presented here, we obtain for the trace of the displacement gradient h^{kk} and for the component $\sigma^{\langle rr\rangle}$ of the deviatoric stress, which is needed in (51),

$$h^{kk} = \begin{cases} 3(a+b) & \text{in } \Omega_\gamma \\ 3a & \text{in } \Omega_\alpha \end{cases} \qquad \text{and} \qquad \sigma^{\langle rr\rangle} = \begin{cases} 0 & \text{in } \Omega_\gamma \\ -4\mu_\alpha\, b & \text{in } \Omega_\alpha \end{cases} \quad (71)$$

with the constants a, b defined in (66) and μ_α denoting the shear modulus of α-iron. Thus, the mole densities of iron, n^α_{Fe} and n^γ_{Fe}, and the chemical potentials can be expressed as functions depending on y^α, y^γ, r_I and r_0. Together with $(49)_1$, (50) and (51) we have derived a system of equations to determine the temporal evolution of these variables.

5.3 A numerical example

In this section, simulation results for the simplified interface-controlled model are presented. For the numerical treatment dimensionless quantities are introduced, which are given by the following relations

$$\hat{t} := \frac{t}{\tau}, \quad \hat{r} := \frac{r}{\overline{r}_0}, \quad \hat{n}_{\mathrm{Fe}} := \frac{n_{\mathrm{Fe}}}{\overline{n}_{\mathrm{Fe}}}, \quad \hat{p} := \frac{p - \overline{p}}{\overline{p}} \quad \text{and} \quad \hat{\mu} := \frac{\overline{n}_{\mathrm{Fe}}}{\overline{p}}\mu. \quad (72)$$

The time scale is chosen as $\tau = 35\,\mathsf{s}$, for the length scale we use a typical austenite grain size of $\overline{r}_0 = 25\,\mu\mathsf{m}$. As reference state we choose a system consisting of pure γ-iron, containing no carbon. Therefore, we set $\overline{n}_{\mathrm{Fe}} = (V^\gamma_m)^{-1}$, where V^γ_m is the molar volume of austenite. The values for the physical quantities used in the simulation are given in Table 1.

Data for the interface mobility M^I_{Fe} can be found e. g. in [7]. There, the authors review different values for the mobility of α-γ interfaces in Fe-C alloys. We take the following value, which, according to the authors, is used successfully in other studies

$$M_{\mathrm{HH}} = 0.058\exp\left(-\frac{140\,\mathsf{kJ\,mol^{-1}}}{RT}\right)\frac{\mathsf{m\,mol}}{\mathsf{J\,s}}. \quad (73)$$

To match the interface mobility M^I_{Fe} to the model used in [7], we choose $M^I_{\mathrm{Fe}} = \overline{n}_{\mathrm{Fe}}M_{\mathrm{HH}}$. Introducing the scales (72), one obtains a nondimensional interface mobility given by

$$\hat{M}^I = \frac{\tau\overline{p}}{\overline{n}^2_{\mathrm{Fe}}\overline{r}_0}M^I_{\mathrm{Fe}}. \quad (74)$$

		ferrite (α-iron)	austenite (γ-iron)	unit
bulk modulus	K	168.9	148.8	10^9 Pa
shear modulus	μ	83.9	75.3	10^9 Pa
molar volume	V_m	7.31	7.24	$10^{-6}\,\mathrm{m^3 mol^{-1}}$
expansion coefficient	δ	2.637	0.588	
molar masses	m_{Fe}	55.847		$\mathrm{g\,mol^{-1}}$
	m_{C}	12.011		$\mathrm{g\,mol^{-1}}$
surface tension	γ	0.5		$\mathrm{N\,m^{-1}}$
pressures	$p_0,\ \overline{p}$	10^5		Pa
gas constant	R	8.3144		$\mathrm{J\,mol^{-1}K^{-1}}$

Table 1: Physical parameters used for the simulations

The results presented in this section are obtained using the software package Mathematica. The simulations are done for a fixed temperature of $T = 1050\,\mathrm{K}$. The initial conditions for the carbon fractions y^α and y^γ are chosen such that a mean carbon concentration of 0.2 mass-% results. As the initial condition for the nondimensional outer radius we use $r_0 = 1$. Since nucleation of a new phase is not considered, we have to start with a positive ferrite fraction and therefore the initial interfacial radius is set to $r_I = 0.99$.

Figure 1 shows the evolution of the site fractions of carbon scaled with the site ratio, ηy, in the γ- and α-phase. The interfacial radius is depicted in Figure 2.

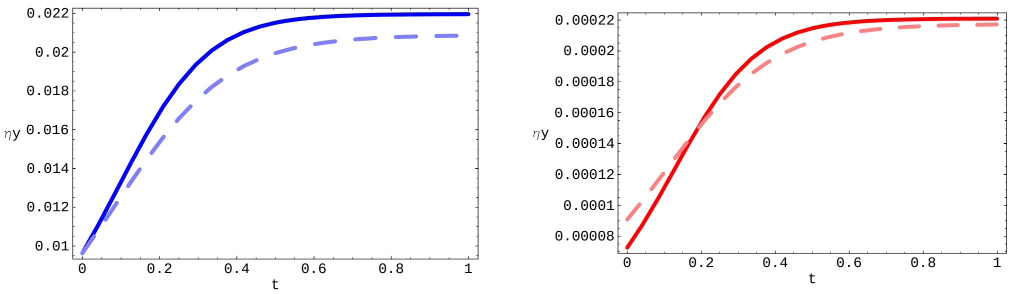

Figure 1: Site fraction ηy in austenite (left) and ferrite (right).

The dashed lines refer to the case where mechanical effects are neglected. One can see a difference in the equilibrium states, which results from the additional mechanical contributions to the chemical potentials μ_{C} and μ_{V}. Furthermore, one recognises an influence on the temporal evolution.

In the case where mechanical effects are neglected, the equilibrium concentrations are independent of the geometry of the grain and the overall carbon content. In contrast to that, the attained equilibria depicted in Figure 1 and 2 depend on the

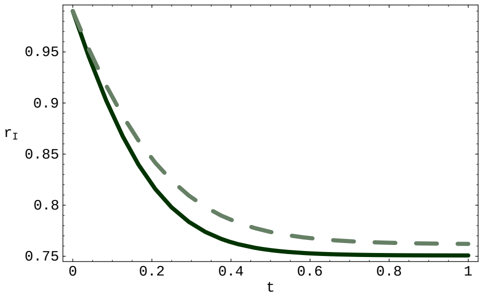

Figure 2: Interfacial radius r_I.

mean carbon concentration and the geometric assumptions for the iron grain made in this section. These properties strongly influence the displacement field, that the chemical potentials depend on and therefore affect the equilibrium states.

The evolution of the outer radius r_0 and of the mass densities ρ^α and ρ^γ is shown in Figure 3. The evolution of these variables results from the eigenstrains caused by the volumetric expansions. In the model neglecting mechanical effects the volume and therefore the radius r_0 is constant.

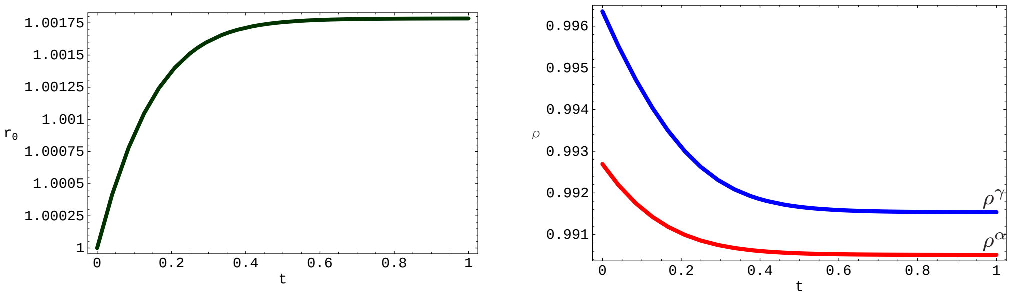

Figure 3: Radius of the grain r_0 and mass densities in ferrite ρ^α and austenite ρ^γ.

A Evaluation of the 2nd law of thermodynamics

A.1 The entropy principle in the bulk

The second law of thermodynamics is a basic physical principle. In this work it is used to derive constitutive functions. It states the existence of a pair of quantities: the entropy density ρs and the entropy flux ϕ^k. They have to satisfy the following balance equation

$$\frac{\partial \rho s}{\partial t} + \frac{\partial}{\partial x^k}(\rho s v^k + \phi^k) = \xi \qquad \text{and} \qquad \xi \geq 0, \tag{75}$$

where ξ is called the entropy production. The non-negativity of ξ represents the second law of thermodynamics and must hold for every thermodynamic process described by the governing PDE system. The equilibrium is defined by $\xi = 0$. A detailed description of the entropy principle can be found e. g. in [1] or [2]. From [1] we take the following representation for the entropy production

$$
\begin{aligned}
\xi = \frac{\partial}{\partial x^k}\left(\phi^k - \frac{q^k}{T} + \frac{1}{T}(j^k_{\mathrm{C}}\mu_{\mathrm{C}} + j^k_{\mathrm{V}}\mu_{\mathrm{V}})\right) - \left(j^k_{\mathrm{C}}\frac{\partial \mu_{\mathrm{C}}/T}{\partial x^k} + j^k_{\mathrm{V}}\frac{\partial \mu_{\mathrm{V}}/T}{\partial x^k}\right) \\
+ q^k\frac{\partial 1/T}{\partial x^k} + \frac{\partial v^m}{\partial x^k}\frac{1}{T}\Bigg[\sigma^{km} - J^{-2/3}(F^{mi}F^{kj} + F^{ki}F^{mj})\frac{\partial \rho\psi}{\partial c^{ij}} \\
+ \delta^{mk}\left(-\rho\psi + n_{\mathrm{C}}\mu_{\mathrm{C}} + n_{\mathrm{V}}\mu_{\mathrm{V}} + \frac{2}{3}J^{-2/3}C^{ij}\frac{\partial \rho\psi}{\partial c^{ij}}\right)\Bigg] \geq 0,
\end{aligned}
\tag{76}
$$

where q^k denotes the heat flux. The remaining quantities are as introduced in the previous sections. The constitutive functions, relating e. g. the diffusion flux to the variables, need to be constructed in such a way that the 2nd law of thermodynamics in terms of the inequality (76) holds for any solution of the PDE system.

The entropy flux in the case of a multi component mixture is defined as

$$
\phi^k := \frac{q^k}{T} - \frac{1}{T}(j^k_{\mathrm{C}}\mu_{\mathrm{C}} + j^k_{\mathrm{V}}\mu_{\mathrm{V}}) \tag{77}
$$

and therefore the first term vanishes. The whole bracket in the last term of (76) must vanish, too. Otherwise it is possible to violate the inequality. This gives the relations

$$
\rho\psi + p = n_{\mathrm{C}}\mu_{\mathrm{C}} + n_{\mathrm{V}}\mu_{\mathrm{V}}, \quad p := -\frac{1}{3}\sigma^{kk} = \rho^2\frac{\partial\hat{\psi}}{\partial\rho} \quad \text{and} \quad t^{ij} = 2\overline{\rho}\frac{\partial\tilde{\psi}}{\partial C^{ij}}. \tag{78}
$$

Equation $(78)_1$ is known as the Gibbs-Duhem equation. Again, we refer to [1] for a derivation of (78). The remaining terms in (76) have the form *flux* × *driving force*. To ensure that the entropy production is nonnegative one can use the following ansatz for the diffusion flux

$$
j^k_{\mathrm{C}} = -M^B\frac{\partial}{\partial x^k}\left(\mu_{\mathrm{C}} - \frac{\eta m_{\mathrm{C}} + m_{\mathrm{Fe}}}{m_{\mathrm{Fe}}}\mu_{\mathrm{V}}\right), \tag{79}
$$

where the identities (7) are used. The constant $M^B > 0$ denotes the bulk mobility of carbon. Since we restrict ourselves to the isothermal case, the temperature gradients in (76) vanish and the inequality $\xi \geq 0$ holds for every thermodynamic process.

A.2 The entropy principle on the interface

The entropy inequality must be satisfied on the interface I, too. The interfacial entropy production ξ_S is given for example in [2] as

$$
T\xi_S = -\rho(v^\nu - w^\nu)[[\psi + \frac{1}{2}(v-w)^2]] + [[\sigma^{ij}(v^i - w^i)]]\nu^j - [[\mu_{\mathrm{C}}j^\nu_{\mathrm{C}} + \mu_{\mathrm{V}}j^\nu_{\mathrm{V}}]] \geq 0. \tag{80}
$$

The term $(v-w)^2/2$ refers to the kinetic energy of the interface, which is supposed to be small and can be neglected. We use the inequality (80) to formulate constitutive relations for the material mole fluxes $\dot{\mathcal{N}}_{\mathrm{Fe}}$ and $\dot{\mathcal{N}}_{\mathrm{C}}$ similar to (79) for the diffusion flux. To this end, we apply the Gibbs-Duhem equation $(78)_1$, introduce the decomposition $\sigma^{ij} = \sigma^{\langle ij\rangle} - p\delta^{ij}$, the definition of the diffusion fluxes (6) and of the material mole fluxes (11), the side condition (3) and the relation $m_{\mathrm{Fe}}\dot{\mathcal{N}}_{\mathrm{Fe}} + m_{\mathrm{C}}\dot{\mathcal{N}}_{\mathrm{C}} = \rho(v^\nu - w^\nu)$, which is a consequence of (5) and (11), and obtain

$$- \dot{\mathcal{N}}_{\mathrm{Fe}}[[\eta\mu_{\mathrm{V}} - \frac{m_{\mathrm{Fe}}}{\rho}\sigma^{\langle ij\rangle}\nu^i\nu^j]] - \dot{\mathcal{N}}_{\mathrm{C}}[[\mu_{\mathrm{C}} - \mu_{\mathrm{V}} - \frac{m_{\mathrm{C}}}{\rho}\sigma^{\langle ij\rangle}\nu^i\nu^j]] \geq 0. \qquad (81)$$

Similar to the entropy principle in the bulk, this inequality has the form of a sum of terms, which can be identified by *flux × driving force*. The inequality can be satisfied if we set

$$\dot{\mathcal{N}}_{\mathrm{Fe}} = -M^I_{\mathrm{Fe}}[[\eta\mu_{\mathrm{V}} - \frac{m_{\mathrm{Fe}}}{\rho}\sigma^{\langle ij\rangle}\nu^i\nu^j]] \quad \text{and} \quad \dot{\mathcal{N}}_{\mathrm{C}} = -M^I_{\mathrm{C}}[[\mu - \frac{m_{\mathrm{C}}}{\rho}\sigma^{\langle ij\rangle}\nu^i\nu^j]] \qquad (82)$$

with positive interface mobilities $M^I_{\mathrm{Fe}}, M^I_{\mathrm{C}}$ for iron and carbon and the chemical potential $\mu := \mu_{\mathrm{C}} - \mu_{\mathrm{V}}$.

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