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## ON A NUMERICAL MODEL OF PHASE TRANSFORMATION IN SUBSTITUTIONAL ALLOYS

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**Abstract.** A new model for the diffusive phase transformation with a finite number  $r$  of substitutional components is based on the application of the Onsager thermodynamic extremal principle; it assumes the interface of finite thickness with finite mobility and solute segregation and drag in the migrating interface. The mathematical analysis leads to a system of PDEs of evolution of the first order (driven by chemical potentials of particular components) for unknown molar fractions  $c_1, \dots, c_r$  ( $c_1 + \dots + c_r = 1$ ) with nonlinear coefficients, including (as an additional variable) an interface displacement rate  $v(c_1, \dots, c_r)$ , evaluated from a nonlocal algebraic equation. Especially in the 1D stationary case (where  $v$  is independent of time) such system degenerates to a system of ODEs; for this case reliable material characteristics at least for a Fe-rich Fe-Cr-Ni system ( $r = 3$ ) from the Montanuniversität Leoben (Austria) are available. The software for transformation and differentiation of a large set of such characteristics (as complicated functions of  $c_1, \dots, c_r$ ) makes use of MAPLE-supported symbolic manipulations. The simulation software has been written in MATLAB; some predicted results can be identified with those obtained by laboratory measurements and practical observations.

**Key words.** Phase transformation, diffusion, interface kinetics, thermodynamic extremal principles, special systems of ODEs, PDEs of evolution, finite difference method.

**AMS subject classifications.** 74N25

**1. Introduction.** Phase transformations represent a decisive mechanism in refinement of microstructure in many materials leading to dramatic enhancement of their mechanical properties. Numerical modelling seems to be not only an important tool in understanding of processes occurring during the phase transformation, simulation based on the reliable

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models can help in design of new advanced materials or provide estimations of the life time of components.

To model diffusional phase transformation, it is necessary to solve the coupled problem of diffusion and interface migration; the calculation scale is typically much lesser than  $1 \mu m$ . Practically all models assume a sharp interface with ortho-equilibrium or para-equilibrium contact conditions; for the review (with many references) see [1]. A more general set of contact conditions at a sharp interface with some finite mobility is studied just in [1]; for the case of substitutional alloys [4] demonstrates how the jumps of chemical potentials can be derived from the Onsager thermodynamic extremal principle of maximum dissipation. The contact conditions influence the kinetics of phase transformation dramatically, thus they are topics of theoretical works on phase transformation (cf. [2]).

We shall consider a closed one-dimensional system with a finite number  $r \in \{2, 3, 4, \dots\}$  of substitutional components with no sources and sinks of vacancies. We can admit  $r = 2$ , although for this case a more simple approach is available (with only one resulting nonlinear ODE or PDE of evolution); in our numerical application we shall need  $r = 3$  for certain Fe-rich Fe-Cr-Ni system (some results for a similar system with a fixed finite interface thickness have been presented in [5]). Two phases,  $\alpha$  and  $\gamma$ , will be separated by a migrating incoherent interface; the  $\alpha \rightarrow \gamma$  transformation will be active. The local chemical composition is described by molar fractions  $c = (c_1, \dots, c_r)$  for particular components:  $c_r = 1 - c_1 - \dots - c_{r-1}$ . The chemical potentials  $\mu_1, \dots, \mu_r$  depend both on  $c_1, \dots, c_r$  and on the coordinate  $x$  directly (for the details see below). The interface of the constant thickness is assumed to move from the left to the right. No deformation at any point due to diffusion or phase transformation, no sources or sinks of vacancies and no stresses in the system (consequently: no mechanical driving force for a coupled process of bulk diffusion and interface migration) will be included into our model.

The following symbols will be used frequently:  $i$  for a component index ( $i \in \{1, \dots, r\}$ ),  $c_i$  for a component concentration,  $j_i$  for a component diffusional flux,  $x$  for a coordinate in the one-dimensional Euclidean space ( $x \in \Omega = \langle 0, H \rangle$ ,  $H$  is a positive real constant),  $t$  for a time coordinate ( $t \in \langle 0, \infty \rangle$ ). The material characteristics are three diffusional



coefficients  $D_i(x)$ , one interface mobility  $M$  and three chemical potentials  $\mu_i(c, x)$ . In the following considerations also the diffusional factor  $A_i = c_i D_i / (RT)$  for the constant  $R = 8314 \text{ J K}^{-1} \text{ mol}^{-1}$  and for certain fixed temperature  $T$  will be useful.

Unlike the heuristic difference approach of [3] and [4], our physical analysis will result in formulation of a boundary value problem for a system of ordinary differential equations, in general of evolution type, more simple in a stationary case. The numerical analysis of such system comes out from finite difference techniques for nonlinear problems.

**2. Derivation of a model from the Onsager principle.** Let us analyze a material sample, using a view of size  $H$ , whose initial position (for  $t = 0$ ) is  $\Omega = \langle 0, H \rangle$ , containing an interface of finite constant thickness  $h$ , whose initial position is  $I = \langle x_R, x_L \rangle$  ( $h = x_R - x_L$ ,  $0 \leq x_R < x_L \leq H$ ,  $h \ll H$  in practice). We shall assume that our view is moving in time from the right to the left (to set positive orientation of such motion) together with our interface (position of  $I$  inside  $\Omega$  is still preserved); a rate  $v$  of such motion depends on  $t$  only (not on  $x$ ). A local coordinate  $\tilde{x}$ , connected with our view, can be calculated from  $x$  easily, applying the substitution  $\tilde{x}(t) = x - u(t)$  where

$$u(t) = \int_0^t v(\tau) d\tau$$

and therefore also  $\dot{\tilde{x}}(t) = -v(t)$ ;  $\dot{\psi}$  denotes a (total) time derivative of a variable  $\psi$  everywhere, similarly  $\psi'$  will (later) denote a derivative with respect to a variable  $x$ . Consequently any integral of type

$$\Psi(t) = \int_{-u(t)}^{H-u(t)} g(x, t) d\tilde{x}$$

for an arbitrary integrable function  $g$  (related to  $\Omega$  in any time  $t$ ) can be simplified as

$$\Psi(t) = \int_0^H g(x, t) dx.$$

In the following considerations the fact that variables are dependent on  $t$  or  $x$  will not be emphasized explicitly (if no risk of misunderstanding exists). An index  $i$  from the set  $\{1, \dots, r\}$  will refer to an arbitrary component of our three-component system, an index  $\rho$  from the set  $\{\alpha, \beta, \gamma\}$  will refer to its arbitrary phase.

The total Gibbs energy of the system is given by

$$G = \frac{1}{\Theta} \int_0^H c_i \mu_i dx$$

$\Theta$  here is a number of mols in a volume unit. Let us assume that all chemical potentials  $\mu_i$  are functions of  $x$  and  $c = (c_1, \dots, c_r)$ , expressed in form

$$\mu_i(x, c) = \sum_{\sigma \in \{\alpha, \beta, \gamma\}} w_\sigma(x) \mu_i^\sigma(c)$$

on  $\Omega$ ;  $w_\alpha$ ,  $w_\beta$  and  $w_\gamma$  here are some weight functions (if  $0 \leq x \leq H$  then  $w_\alpha(x) \geq 0$ ,  $w_\beta(x) \geq 0$ ,  $w_\gamma(x) \geq 0$ ,  $w_\alpha(x) + w_\beta(x) + w_\gamma(x) = 1$ ) and  $\mu_i^\alpha$ ,  $\mu_i^\beta$  and  $\mu_i^\gamma$  are functions of  $c$  only (not of  $x$  or  $t$  directly).

The conservation of mass for every component  $c_i$  is guaranteed by the Fick law  $\dot{c}_i + j'_i/\Theta = 0$ . Thus, the differentiation of  $G$  in time gives

$$\begin{aligned} \dot{G} &= \frac{1}{\Theta} \sum_{k=1}^r \int_0^H \dot{c}_k \mu_k dx + \frac{1}{\Theta} \sum_{k=1}^r \int_0^H c_k \dot{\mu}_k dx \\ &= - \sum_{k=1}^r \int_0^H j'_k \mu_k dx + \frac{1}{\Theta} \sum_{k=1}^r \int_0^H c_k \dot{\mu}_k dx \end{aligned}$$

and with respect (in any time) to boundary conditions  $j_i(0, t) = j_i(H, t) = 0$  (no diffusion boundary fluxes for our view are allowed)

$$\dot{G} = \frac{1}{\Theta} \sum_{k=1}^r \int_0^H j_k \mu'_k dx + \frac{1}{\Theta} \sum_{k=1}^r \int_0^H c_k \dot{\mu}_k dx.$$

But we have also

$$\dot{\mu}_i = \sum_{\sigma \in \{\alpha, \beta, \gamma\}} \left( \dot{\mu}_i^\sigma w_\sigma + \mu_i^\sigma w'_\sigma \dot{x} \right) = \sum_{\sigma \in \{\alpha, \beta, \gamma\}} \dot{\mu}_i^\sigma w_\sigma - v \sum_{\sigma \in \{\alpha, \beta, \gamma\}} \mu_i^\sigma w'_\sigma$$

and the well-known Gibbs-Duhem condition for any phase on  $\Omega$

$$\sum_{k=1}^r c_k \dot{\mu}_k^\rho = 0$$

gives

$$\sum_{k=1}^r c_k \dot{\mu}_k = -v \sum_{k=1}^r \sum_{\sigma \in \{\alpha, \beta, \gamma\}} \mu_k^\sigma w'_\sigma$$

and consequently

$$\dot{G} = \sum_{k=1}^r \int_0^H j_k \mu'_k dx - \frac{v}{\Theta} \sum_{k=1}^r \sum_{\sigma \in \{\alpha, \beta, \gamma\}} \int_0^H c_k \mu_k^\sigma w'_\sigma dx.$$

Since  $w'_\rho = 0$  outside  $I$  ( $w_\alpha = 1$  for  $x < x_L$ ,  $w_\gamma = 1$  for  $x > x_R$ ,  $w_\rho = 0$  otherwise), we can write finally

$$\dot{G} = \sum_{k=1}^r \int_0^H j_k \mu'_k dx - \frac{v}{\Theta} \sum_{k=1}^r \sum_{\sigma \in \{\alpha, \beta, \gamma\}} \int_{x_L}^{x_R} c_k \mu_k^\sigma w'_\sigma dx.$$

The rate of the energy dissipation due to bulk diffusion and interface migration can be evaluated as

$$Q = \frac{1}{2} \sum_{k=1}^r \int_0^H (j_k/A_k - 2\lambda) j_k dx + \frac{1}{2} v^2/M.$$

We shall see that the Lagrange multiplier  $\lambda$  forces the natural condition of zero sum of diffusional fluxes.

By the Onsager thermodynamic extremal principle the kinetics of the system corresponds to the condition of zero variation of  $\dot{G} + Q$  with respect to all variables. For all admissible  $\tilde{j}_1, \tilde{j}_2, \tilde{j}_3, \tilde{v}$  and  $\tilde{\lambda}$  we have variations

$$D(\dot{G} + Q)(\tilde{j}_1, \tilde{j}_2, \tilde{j}_3) = \sum_{k=1}^r \int_0^H \tilde{j}_k \mu'_k dx + \sum_{k=1}^r \int_0^H (j_k \tilde{j}_k / A_k) dx = 0,$$

$$D(\dot{G} + Q)(\tilde{v}) = -\frac{\tilde{v}}{\Theta} \sum_{k=1}^r \sum_{\sigma \in \{\alpha, \beta, \gamma\}} \int_{x_L}^{x_R} c_k \mu_k^\sigma w'_\sigma dx + \tilde{v} v / M = 0,$$

$$DQ(\tilde{\lambda}) = -\sum_{k=1}^r \int_0^H j_k \tilde{\lambda} = 0.$$

Thus, we receive (for every  $x \in \Omega$ )

$$\mu'_i + j_i / A_i + \lambda = 0, \quad \sum_{k=1}^r j_k = 0$$

and moreover

$$v = \frac{M}{\Theta} \sum_{k=1}^r \sum_{\sigma \in \{\alpha, \beta, \gamma\}} \int_{x_L}^{x_R} c_k \mu_k^\sigma w'_\sigma dx.$$

Let us mention some more consequences of the Gibbs-Duhem conditions. We have

$$\sum_{k=1}^r c_k \dot{\mu}_k = \sum_{k=1}^r \sum_{\sigma \in \{\alpha, \beta, \gamma\}} c_k \dot{\mu}_k^\sigma w_\sigma = 0$$

and

$$v \sum_{k=1}^r c_k \mu_k^{\rho'} = - \sum_{k=1}^r c_k \dot{\mu}_k^{\rho} = 0$$

on  $\Omega$ . Moreover,

$$v \sum_{k=1}^r c_k \mu_k' = v \sum_{k=1}^r \sum_{\sigma \in \{\alpha, \beta, \gamma\}} c_k \mu_k^{\sigma'} w_s + v \sum_{k=1}^r \sum_{\sigma \in \{\alpha, \beta, \gamma\}} c_k \mu_k^s w'_\sigma = v \sum_{k=1}^r \sum_{\sigma \in \{\alpha, \beta, \gamma\}} c_k \mu_k^{\sigma} w'_\sigma$$

on  $\Omega$ ; in particular,

$$v \sum_{k=1}^r c_k \mu_k' = 0$$

outside  $I$ . The same is true even on  $I$  in case  $v = 0$ ; otherwise we obtain an alternative explicit formula for the evaluation of  $v$ ,

$$v = \frac{M}{\Theta} \sum_{k=1}^r \int_{x_L}^{x_R} c_k \mu_k' dx.$$

(Nevertheless, for practical calculations its original form seems to be more useful.)

The variable  $\lambda$  occurs only in the first equation and can be eliminated: multiplying this equation by  $A_i$ , we obtain  $\lambda A_i = -j_i - A_i \mu_i'$ . The sum of all such equations with respect to the second equation gives

$$\lambda \sum_{k=1}^r A_k = - \sum_{k=1}^r A_k \mu_k' ;$$

this results

$$\lambda = - \sum_{k=1}^r A_k \mu'_k / \sum_{l=1}^r A_l$$

and consequently

$$j_i = -A_i \mu'_i - A_i \lambda = A_i (-\mu'_i + \sum_{k=1}^r A_k \mu'_k / \sum_{l=1}^r A_l) = -A_i \sum_{k=1}^r A_k (\mu'_i - \mu'_k) / \sum_{l=1}^r A_l.$$

Let us now make some remarks to limit cases of practical interest. If  $j_i$  is bounded (this is guaranteed e.g. by the assumption of boundedness of  $\partial c_i / \partial t$  – this fact can be verified using the integration of the original formula for  $j_i$  from the Fick law by  $x$ ) then, integrating the relation  $\mu'_i = -\lambda - j_i / A_i$  from  $x_L$  to  $x_R$  with the result

$$\mu_i(x_R) - \mu_i(x_L) = - \int_{x_L}^{x_R} \lambda \, dx - \int_{x_L}^{x_R} (j_i / A_i) \, dx,$$

we can conclude that, substituting all  $A_i$ , supposed to have positive lower bounds (which forces non-zero concentrations), by  $A_i / \varepsilon$  with a sequence of decreasing positive  $\varepsilon$ , the limit passage  $\varepsilon \rightarrow 0$  guarantees

$$\lim_{\varepsilon \rightarrow 0} (\mu_i(x_R) - \mu_i(x_L)) = - \int_{x_L}^{x_R} \lambda \, dx$$

because

$$\lim_{\varepsilon \rightarrow 0} \left| \int_{x_L}^{x_R} (\varepsilon j_i / A_i) \, dx \right| \leq \lim_{\varepsilon \rightarrow 0} \int_{x_L}^{x_R} |\varepsilon j_i / A_i| \, dx \leq \kappa h \lim_{\varepsilon \rightarrow 0} \varepsilon = 0$$

with some positive constant  $\kappa$ . The integral of  $\lambda$  from  $x_L$  to  $x_R$  is finite (non-zero in general), but the same for every  $i$ ; in the particular case this property can be seen from the graph,



presented in [5]. However, the similar conclusion could be done also for the ideal model of very thin interface with  $h \rightarrow 0$  because

$$\lim_{h \rightarrow 0} \left| \int_{x_L}^{x_R} (j_i/A_i) dx \right| \leq \lim_{h \rightarrow 0} \int_{x_L}^{x_R} |j_i/A_i| dx \leq \kappa \lim_{h \rightarrow 0} h = 0$$

(cf. FIG. 4.3).

**3. A stationary case.** Most experiments with  $\alpha \rightarrow \gamma$  transformations verify the hypothesis that (after some time) the process obtains steady-state properties – the quantities  $v$  and  $c$  become constant in time. The diffusional fluxes  $j_i$  on  $I$  are then able to be related to the concentrations  $c_i$  as  $j_i = v(c_i - c_i^\times)$  where  $c_i^\times$  are some prescribed concentrations in the phase  $\gamma$  far from the interface; the integral expression for the evaluation of  $v$  stays unchanged. Especially in the phase  $\alpha$  no concentration profiles exist – the chemical composition is given by  $c_i^\times$ .

Let us introduce the decomposition  $\mu_i^\rho(c) = \mu_{0i}^\rho + RT \ln c_i + \varphi_i^\rho(c)$  where  $\mu_{0i}^\rho$  and  $RT$  are constants and  $\varphi_i^\rho$  are functions of  $c$  (not dominant, but rather complicated in practice). Then

$$\mu'_i = \sum_{\sigma \in \{\alpha, \beta, \gamma\}} (w'_\sigma \mu_i^\sigma + w_\sigma \mu_i^{\sigma'})$$

obtains the form

$$\mu'_i = \hat{\mu}_i + RT(c'_i/c_i) + \sum_{l=1}^r \hat{\varphi}_{il} c'_l,$$

applying the brief notation

$$\hat{\mu}_i = \sum_{\sigma \in \{\alpha, \beta, \gamma\}} w'_\sigma \left( \mu_{0i}^\sigma + \sum_{l=1}^r \varphi_{i,l}^\sigma c'_l \right), \quad \hat{\varphi}_{il} = \sum_{\sigma \in \{\alpha, \beta, \gamma\}} w_\sigma \sum_{l=1}^r \varphi_{i,l}$$

where  $\varphi_{i,l}$  means  $\partial\varphi_i/\partial c_l$ , etc.

By means of  $D_i$  (instead of  $A_i$ ) we are able to express diffusional fluxes as

$$j_i = -c_i D_i / (RT) \left( \sum_{k=1}^r c_k D_k (\mu'_i - \mu'_k) \right) / \left( \sum_{l=1}^r c_l D_l \right).$$

The notation  $\zeta_i = D_i/D$ ,  $\eta = \sum_{l=1}^r \zeta_l c_l$  with some chosen standard value of a diffusional coefficient  $D$  enables us to simplify this formula into the form

$$j_i = -c_i \zeta_i D / (RT) \sum_{k=1}^r (c_k \zeta_k / \eta) (\mu'_i - \mu'_k).$$

Inserting above calculated  $\mu'_i$  (and dividing by  $-\zeta_i D$ ), we obtain

$$\begin{aligned} -j_i / (\zeta_i D) &= c_i / (RT) \left( \hat{\mu}_i + RT(c'_i/c_i) + \sum_{l=1}^r \hat{\varphi}_{il} c'_l \right) \\ &\quad - c_i / (RT) \sum_{k=1}^r \left( (c_k \zeta_k / \eta) \hat{\mu}_k + RT(c_k \zeta_k / \eta) (c'_k/c_k) + (c_k \zeta_k / \eta) \sum_{l=1}^r \hat{\varphi}_{kl} c'_l \right) \end{aligned}$$

and with help of the some additional notation  $\bar{\mu}_i = \hat{\mu}_i - \sum_{k=1}^r (c_k \zeta_k / \eta) \hat{\mu}_k$ ,  $\bar{\varphi}_{ik} = \hat{\varphi}_{ik} - \sum_{l=1}^r (c_l \zeta_l / \eta) \hat{\varphi}_{lk}$  finally

$$-j_i / (\zeta_i D) = c'_i - c_i / \eta + c_i \bar{\mu}_i / (RT) + c_i \sum_{k=1}^r (\bar{\varphi}_{ik} / RT) c'_k.$$

But we also know that

$$-j_i / (\zeta_i D) + v(c_i - c_i^x) / (\zeta_i D) = 0;$$

this results

$$c'_i + c_i \sum_{k=1}^r (-\zeta_k/\eta + \bar{\varphi}_{ik}/(RT)) c'_k + (\bar{\mu}_i/(RT) + v/(\zeta_i D)) c_i = v c_i^\times / (\zeta_i D).$$

Evidently,  $c_1 + \dots + c_r = 1$ , and thus  $c'_r = -c'_1 - \dots - c'_{r-1}$ . This enables us to remove the last  $r$ -th equation and to express  $c_r$  (including its derivative) in first two equations by means of remaining concentrations. In this way for  $i < r$  we receive

$$c'_i + \sum_{k=1}^2 B_{ik} c'_k + K_i c_i = F_i$$

where  $B_{ik} = c_i(\zeta_3 - \zeta_k)/\eta + (\bar{\varphi}_{ik} - \bar{\varphi}_{i3})/(RT)$ ,  $K_i = \bar{\mu}_i/(RT) + v/(\zeta_i D)$ ,  $F_i = v c_i^\times / (\zeta_i D)$ . With help of the notation this system of equations can be rewritten in a matrix form  $(\mathbf{I} + \mathbf{B})\bar{c}' + \mathbf{K}\bar{c} = F$  where  $\mathbf{I}$  is an identity matrix of order  $r - 1$ ,  $\mathbf{B}$  is a square matrix of order  $r - 1$  compound from elements  $B_{11}, \dots, B_{1r-1}, \dots, B_{r-11}, B_{r-1r-1}$ ,  $\mathbf{K}$  is a diagonal square matrix compound from diagonal elements  $K_1, \dots, K_{r-1}$  and  $F$  is a column vectors of size  $r - 1$  compound from elements  $F_1, \dots, F_{r-1}$ .

**4. Numerical simulation.** In all cases of practical interest (even in a very simplified case of all constant  $\mu_{0i}$  and zero  $\phi_i$ ) the exact solution of the derived system is not known. The analysis of existence and uniqueness of a solution is not trivial; the crucial difficulty is that reasonable bounds for very complicated functions  $\phi_i$  and their derivatives are not available. Such deterministic functions, whose formulations come from extensive theoretical and experimental research, reflect a lot of physical phenomena (as ferromagnetism), not discussed in this paper, and their validity, guaranteed with high precision e. g. for  $c_1, c_2 \ll 1$  and  $c_3$  close to 1 for the above mentioned Fe-rich systems, is not allowed to be extended to quite other (but realistic) systems. However, for simulations of phase transformations some robust numerical scheme is needed. In addition, such scheme must respect that all diffusion coefficients  $D_i(x)$  change their values on  $I$  very rapidly.

The Crank-Nicholson scheme on  $I$  gives

$$\left( \mathbf{I} + \bar{\mathbf{B}}^s + \frac{\Delta}{2} \bar{\mathbf{K}}^s \right) \bar{c}^s = \left( \mathbf{I} + \bar{\mathbf{B}}^s - \frac{\Delta}{2} \bar{\mathbf{K}}^s \right) \bar{c}^{s-1} + \bar{F}^s;$$

here  $\Delta$  means a calculation step and  $\psi^s$  is briefly used instead of  $\psi(s\Delta)$  for any function  $\psi(x)$  everywhere on  $\Omega$  and  $s \in \{1, \dots, m\}$ ,  $m = h/\Delta$  (therefore  $c'((s+1/2)\Delta) \approx (c^s - c^{s-1})/\Delta$ ). At the start of all calculations both matrices  $\bar{\mathbf{B}}^s = (\mathbf{B}^s + \mathbf{B}^{s-1})/2$ ,  $\bar{\mathbf{K}}^s = (\mathbf{K}^s + \mathbf{K}^{s-1})/2$  and a vector  $\bar{F}^s = (F^s + F^{s-1})/2$  are set using the assumption that  $c_i = c_i^x$  (no better information is available); this starts an iterative procedure of evaluation of  $\bar{c}^1, \bar{c}^2, \dots, \bar{c}^m$  and also of an integral sum

$$v = \frac{M\Delta}{\Theta} \sum_{k=1}^r \sum_{\sigma \in \{\alpha, \beta, \gamma\}} \sum_{s=1}^{m-1} c_k^s \mu_k^{\sigma s} w'_\sigma(s\Delta)$$

where  $\mu_k^{\sigma s}$  denotes the value of  $\mu_k^\sigma$  in  $c^s$  (we have  $w'_\sigma(0) = w'_\sigma(m\Delta) = 0$ ), correction of  $\mathbf{B}^1, \dots, \mathbf{B}^m$ , of  $\mathbf{K}^1, \dots, \mathbf{K}^m$  and of  $F^1, \dots, F^m$ , etc.

Outside  $I$  (where  $H \gg h$ ) the real distributions of concentrations are typically similar to (but not exactly identical with) exponential curves: the first additive term in  $K_i$  is equal to zero, the right-hand side of the whole system of ODEs is constant, the (non-constant) matrix  $\mathbf{B}^s$  is not far from diagonal (neglecting all terms of type  $\hat{\varphi}_{ik}$ ), thus the eigenvalue analysis for  $(\mathbf{I} + \bar{\mathbf{B}}^s)^{-1} \bar{\mathbf{K}}^s$  can be useful to substitute approximate solutions from the Crank-Nicholson scheme. In more details: in general we can seek for  $\tilde{c}^s(x) = \tilde{c}^{s0} + \tilde{c}^{s1}(x)$  where  $\tilde{c}^{s0} = (\bar{\mathbf{K}}^s)^{-1} \bar{F}^s$ ,  $\tilde{c}^{s1}(x) = \mathbf{V}^s \mathbf{E}^s(x) \kappa^s$ ,  $x \in \langle h + (s-1)\Delta, h + s\Delta \rangle$  ( $\Delta$  is a calculation step again, although it may differ from  $\Delta$  applied on  $I$ ),  $\mathbf{V}^s$  is some square matrix of order  $r-1$ ,  $\kappa^s$  is some column vector of size  $r-1$ ,  $\mathbf{E}^s(x)$  is certain diagonal square matrix of order  $r-1$  compound from elements  $E_i^s(x) = \exp(-\lambda_i^s(x - (s-1)\Delta))$  and  $\lambda_i^s$  are up to now unknown parameters. Consequently  $\tilde{c}^{s'}(x) = -\mathbf{V}^s \mathbf{\Lambda}^s(x) \kappa^s$  where  $\mathbf{\Lambda}^s$  is a square matrix of order  $r-1$  compound from above mentioned parameters  $\lambda_i^s$ . Let us assume that  $\tilde{c}^{s1}(x)$  satisfies a system



$(\mathbf{I} + \bar{\mathbf{B}}^s) \tilde{c}^{s1'}(x) = -\bar{\mathbf{K}}^s \tilde{c}^{s1}(x)$ . Then we have  $-(\mathbf{I} + \bar{\mathbf{B}}^s) \mathbf{V}^s \mathbf{\Lambda}^s \mathbf{E}^s(x) \kappa^s = -\bar{\mathbf{K}}^s \mathbf{V}^s \mathbf{E}^s(x) \kappa^s$  and consequently  $\mathbf{V}^s \mathbf{\Lambda}^s \mathbf{E}^s(x) \kappa^s = (\mathbf{I} + \bar{\mathbf{B}}^s)^{-1} \bar{\mathbf{K}}^s \mathbf{V}^s \mathbf{E}^s(x) \kappa^s$ ; in other words:  $\lambda_i^s$  are eigenvalues and two columns of  $\mathbf{V}^s$  are orthonormal eigenvectors of  $(\mathbf{I} + \bar{\mathbf{B}}^s)^{-1} \bar{\mathbf{K}}^s$ . It is natural to prescribe  $\bar{c}^{s-1} = \tilde{c}^s(h + (s-1)\Delta)$  to calculate  $\kappa^s$ , following the aim to obtain  $\bar{c}^s = \tilde{c}^s(h + s\Delta)$ . From two corresponding conditions  $\bar{c}^{s-1} = \tilde{c}^{s0} + V^s \kappa^s$ ,  $\bar{c}^s = \tilde{c}^{s0} + V^s \mathbf{E}_\Delta^s \kappa^s$  with a diagonal square matrix  $\mathbf{E}_\Delta^s$  consisting of elements  $E_{\Delta i}^s = \exp(-\lambda_i^s \Delta)$  we receive  $\kappa^s = V^{sT}(\bar{c}^{s-1} - \tilde{c}^{s0})$  and finally  $\bar{c}^s = \tilde{c}^{s0} + V^s \mathbf{E}_\Delta^s V^{sT}(\bar{c}^{s-1} - \tilde{c}^{s0})$ . Especially outside  $I$  no evaluation of  $\tilde{c}^{s0}$  is needed because  $\tilde{c}^{s0} = (\bar{\mathbf{K}}^s)^{-1} F^s = \bar{c}^\times$  with  $\bar{c}^\times = (c_1^\times, c_2^\times)$  and the whole calculation of  $\bar{c}^s$  becomes rather cheap.

All our numerical calculations make use of the original software code, runnable in each standard MATLAB environment (with no special requirements to additional toolboxes or FEMLAB compatibility). Only the automatic code generator of algebraic expressions for  $\mu_i$  evaluation (not described in details here) needs MAPLE-supported symbolic differentiation.

Usually the diffusional coefficients  $D_i^\alpha$  and  $D_i^\gamma$  for the phases  $\alpha$  and  $\gamma$  are known; the same is true for the diffusive coefficients  $D_i^\beta$ , corresponding to an ideal liquid state  $\beta$  of material. However, such diffusive coefficients  $D_i^\beta$  are correct just in the interface center  $x_C = (x_L + x_R)/2$ . The diffusional coefficients  $D_i$  inside the interface ( $x_L < x < x_R$ ) have to be interpolated applying the formula

$$\ln D_i(x) = \sum_{\sigma \in \{\alpha, \beta, \gamma\}} w_\sigma(x) \ln D_i^\sigma;$$

weight functions  $w^\sigma(x)$  here are cubic Hermite interpolations splines given by their values  $w_\alpha(x_L) = w_\gamma(x_R) = 1$ ,  $w_\alpha(x_C) = w_\alpha(x_R) = w_\gamma(x_C) = w_\gamma(x_L) = 0$ ,  $w_\alpha'(x) = w_\gamma'(x) = 0$  for all nodes  $x \in \{x_L, x_C, x_R\}$  and  $w_\beta(x) = 1 - w_\alpha(x) - w_\gamma(x)$  for each  $x \in I$ . The formulation of 3 chemical potentials can be done in the similar way: instead of  $D_i^\sigma$  we know constants  $\mu_{0i}^\sigma$  (as we have explained in the previous section), functions  $\ln$  are missing.

As a typical example, let us consider the three-component ( $r = 3$ ) Fe-rich Fe-Cr-Ni system with the interface thickness  $h = H/2 = 5.10 \cdot 10^{-10}$  m (the value of  $H$  must be supplied for the postprocessing) for the temperature  $T = 1030$  K;  $\Theta = 0.0000072$  mol m $^{-3}$ .

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The values of diffusive coefficients can be transformed from those applied in [4], p. 965:  $D_3^\alpha = 0.00016e^{-24000/(RT)}$ ,  $D_3^\beta = 0.0003e^{-155/(RT)}$ ,  $D_3^\gamma = 0.00007e^{-28600/(RT)}$ , all in  $\text{m}^2/\text{s}$ ; completed by  $D_1^\alpha = 2D_3^\alpha$ ,  $D_1^\beta = 2D_3^\beta$ ,  $D_1^\gamma = 5D_3^\gamma$ ,  $D_2^\alpha = 0.3D_3^\alpha$ ,  $D_2^\beta = 0.3D_3^\beta$ ,  $D_2^\gamma = 0.5D_3^\gamma$ ; to derive dimensionless factors  $\zeta_i$ , we can set  $D = D_3^\alpha$ . Three chemical potentials in all phases are given by  $\mu_{01}^\alpha = -38061.5$ ,  $\mu_{01}^\beta = -25811.1$ ,  $\mu_{01}^\gamma = -30939.3$ ,  $\mu_{02}^\alpha = -42880.4$ ,  $\mu_{02}^\beta = -40079.5$ ,  $\mu_{02}^\gamma = -46810.5$ ,  $\mu_{03}^\alpha = -43591.6$ ,  $\mu_{03}^\beta = -38310.3$ ,  $\mu_{03}^\gamma = -44061.8$ , all in  $\text{J/mol}$ ; in this case the temperature  $T = 1030 \text{ K}$  has been set a priori, as  $\mu_{0i}$  are rather complicated functions of  $T$ . All functions  $\varphi_i^\alpha$  and  $\varphi_i^\gamma$  are available for our Fe-Cr-Ni system as the research outputs from the Mountainuniversität Leoben. Unfortunately, their original calculation formulae are very long (containing more than 1500 FORTRAN program lines) and include a lot of additive terms of power-law types (...)  $c_i^\theta$  and (...)  $c_i^\theta \ln c_i$  with  $\theta \in \{0, 1, \dots, 25\}$ . Moreover, the resarch team in Leoben is still working on the testing, improvement and generalization of these formulae. Therefore it was necessary to prepare a special MAPLE- and MATLAB-based software to analyse such formulae, to decompose them into logical parts and to derive some algorithms for the (not very expensive) evaluation of  $\varphi_i$  and (using the symbolic differentiation) of  $\varphi_{i,k}$ . For an ideal liquid we can suppose  $\varphi_i^\beta = 0$ . We shall start with  $c_1^\alpha = 0.001$ ,  $c_2^\alpha = 0.019$  and  $c_3^\alpha = 0.98$ .

For such data the final distributions of concentrations of Cr, Ni and Fe have been obtained after several iterative steps; the results are evident from FIG. 4.1 where these distributions in the left column are completed by the distributions of corresponding chemical potentials  $\mu_i$  (evaluated from above mentioned complicated formulae). FIG. 4.2, generated by automatically restarted calculations for various values of  $h$  and  $T$ , shows that i) the increasing  $h$  causes that the temperature corresponding to  $v = 0$  is increasing, too, which corresponds to practical experience, ii) the ad hoc difference model with  $h \rightarrow 0$  (from [4]) is only a rough approximation of reality in case of some non-negligible finite thickness  $h$ . FIG. 4.3, generated by automatically restarted calculations for 41 values of  $h$ , shows maximal absolute values of differences of chemical potentials (interface jumps) evaluated for  $\mu(x_L)$  and  $\mu(x_R)$ : the upper curve is valid for Cr, the central one for Fe, the lower one for Ni.

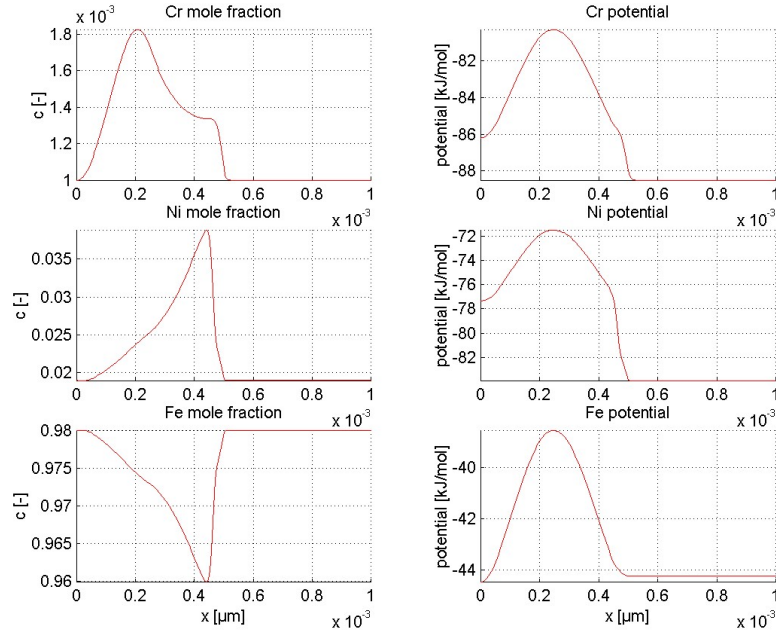


FIG. 4.1. Molar fractions and chemical potentials.

These values vanish in practice only for very low thicknesses  $h$  (exactly in the limit case  $h \rightarrow 0$ ).

**5. A non-stationary case.** Although in all numerical experiments we have paid attention only to a stationary case, let us revise what happens in case that the simplifying assumption  $\partial c_i / \partial t \approx 0$  is not acceptable. Let us remind that a generalized version of a relation between  $c_i$  and  $j_i$  from the preceding section is  $\partial c_i / \partial t - v c_i' + j_i' = 0$  with  $j_i(0) = 0$ .

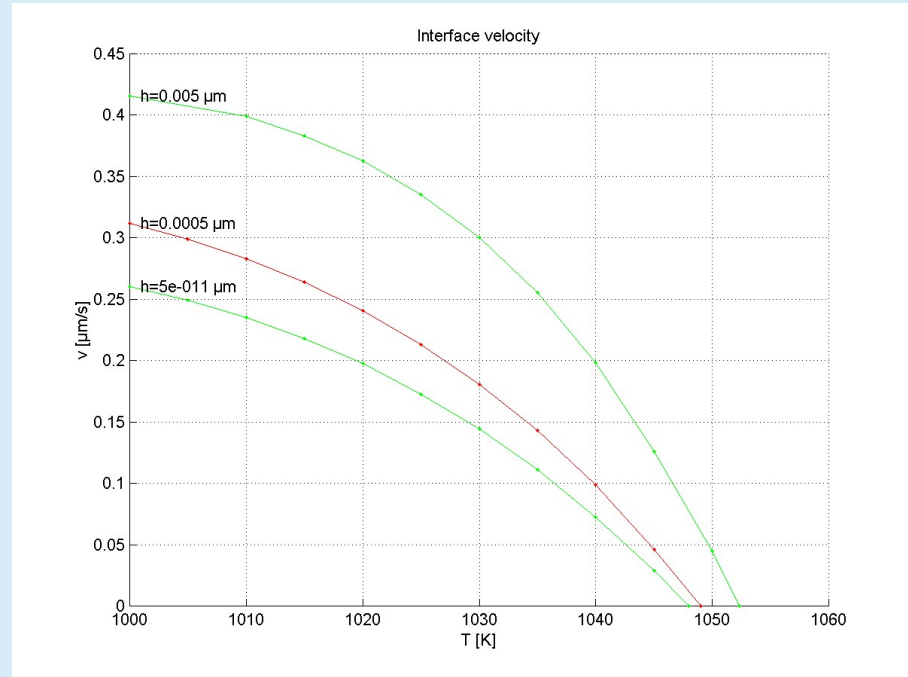


FIG. 4.2. Interface velocity  $v$  as a function of  $h$  and  $T$ .

Integrating this equation with respect to  $x$ , we obtain  $C_i - v(c_i - c_i^x) + j_i = 0$  with

$$C_i(x) = \int_0^x (\partial c_i(\xi)/\partial t) d\xi.$$



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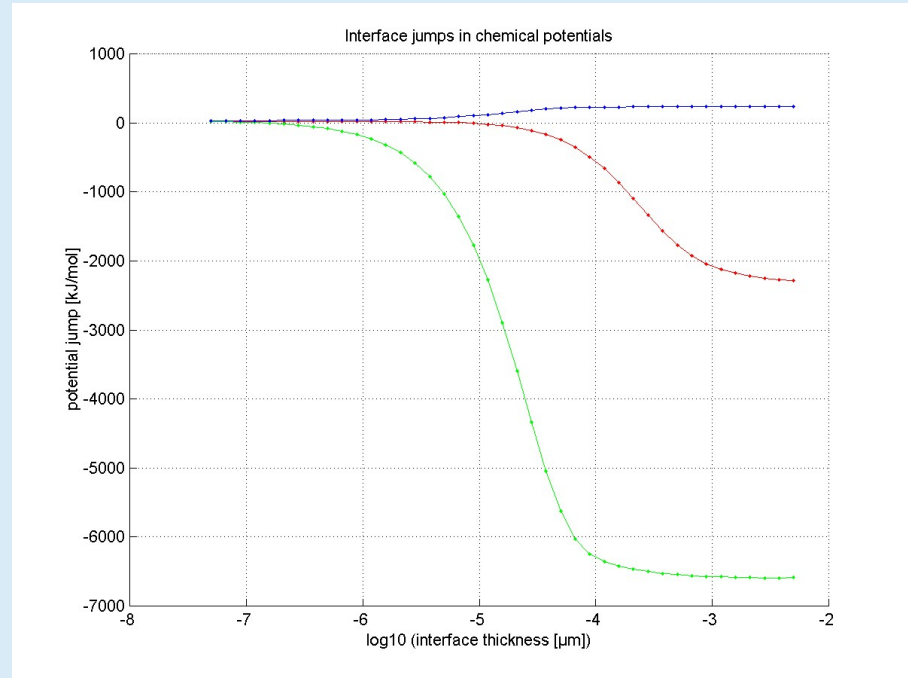


FIG. 4.3. Interface potential jumps for Cr, Ni, Fe as functions of  $h$ .

Indeed, neglecting  $C_i$ , we come back to our original relation for a stationary case.

We shall try to sketch a possible way of generalization of our stationary calculations. In a stationary case we have verified that  $\omega_i = -j_i/(\zeta_i D)$  is a (rather complicated) function of  $c$  and  $c'$ , independent of  $D$  (but still dependent on dimensionless factors  $\zeta_1, \dots, \zeta_{r-1}$ ); then

we have studied in details a relation of type  $\omega_i + L_i c_i = L_i c_i^\times$  with  $L_i = v/(\zeta_i D)$  (later we shall need also a diagonal square matrix  $\mathbf{L}$  compound from  $L_1$  and  $L_2$ ). This relation can be now generalized easily: we obtain

$$\omega_i + L_i \partial C_i / \partial t + L_i c_i = L_i c_i^\times.$$

The Crank-Nicholson scheme in time generates

$$(c_i^q + c_i^{q-1})/2 + L_i (C_i^q - C_i^{q-1})/\tau + L_i (c_i^q + c_i^{q-1})/2 = L_i c_i^\times;$$

here  $\tau$  is a constant time step, upper indices  $q$  correspond to  $t = q\tau$  similarly to indices  $s$  corresponding to  $x = s\Delta$ , etc. The following considerations can be done for an arbitrary integer  $q$ .

For the full discretization (both in  $x$  and in  $t$ ) we must construct an integral sum on  $\Omega$

$$C_i^{qs} = \frac{\Delta}{2} \left( c_i^{q0} + 2 \sum_{p=1}^{s-1} c_i^{qp} + c_i^{qs} \right);$$

it is natural to set  $c_i^{q0} = c_i^\times$ . Let us try to come to formally analogous results to those derived in a stationary case. We shall evidently need some  $\bar{\mathbf{B}}^{qs} = (\mathbf{B}^{qs} + \mathbf{B}^{q s-1} + \mathbf{B}^{q-1 s} + \mathbf{B}^{q-1 s-1})/4$ ,  $\bar{\mathbf{K}}^{qs} = (\mathbf{K}^{qs} + \mathbf{K}^{q s-1} + \mathbf{K}^{q-1 s} + \mathbf{B}^{q-1 s-1})/4$  and  $\bar{\mathbf{F}}^{qs} = (\mathbf{F}^{qs} + \mathbf{F}^{q s-1} + \mathbf{F}^{q-1 s} + \mathbf{F}^{q-1 s-1})/4$ . Let us notice that an upper index  $q$  is necessary even for  $\mathbf{F}$  because it depends on  $v^q$  that must be evaluated in any time  $q\tau$ ; the same is true for  $\mathbf{L}$ :  $\bar{\mathbf{L}}^{qs} = (\mathbf{L}^{qs} + \mathbf{L}^{q s-1} + \mathbf{L}^{q-1 s} + \mathbf{L}^{q-1 s-1})/4$ . Applying the same approach as in a stationary case (and omitting technical details), we receive

$$\begin{aligned} & \frac{1}{2} \left( \mathbf{I} + \bar{\mathbf{B}}^{qs} + \frac{\Delta}{2} \bar{\mathbf{K}}^{qs} \right) (\bar{c}^{qs} + \bar{c}^{q-1 s}) + \frac{\Delta}{2\tau} \bar{\mathbf{L}}^{qs} (\bar{c}^{qs} - \bar{c}^{q-1 s}) + \frac{\Delta}{\tau} \bar{\mathbf{L}}^{qs} \sum_{p=1}^{s-1} (\bar{c}^{qp} - \bar{c}^{q-1 p}) \\ & = \frac{1}{2} \left( \mathbf{I} + \bar{\mathbf{B}}^{qs} - \frac{\Delta}{2} \bar{\mathbf{K}}^{qs} \right) (\bar{c}^{q s-1} + \bar{c}^{q-1 s-1}) + \bar{\mathbf{F}}^{qs}. \end{aligned}$$

This can be (multiplied by 2) rearranged as

$$\left( \mathbf{I} + \bar{\mathbf{B}}^{qs} + \frac{\Delta}{2} \bar{\mathbf{K}}^{qs} + \frac{\Delta}{\tau} \bar{\mathbf{L}}^{qs} \right) \bar{c}^{qs} = \left( \mathbf{I} + \bar{\mathbf{B}}^{qs} - \frac{\Delta}{2} \bar{\mathbf{K}}^{qs} \right) \bar{c}^{q^{s-1}} + \tilde{F}^{qs}$$

where

$$\begin{aligned} \tilde{F}^{qs} = & \bar{F}^{qs} - \left( \mathbf{I} + \bar{\mathbf{B}}^{qs} + \frac{\Delta}{2} \bar{\mathbf{K}}^{qs} - \frac{\Delta}{\tau} \bar{\mathbf{L}}^{qs} \right) \bar{c}^{q-1s} \\ & + \left( \mathbf{I} + \bar{\mathbf{B}}^{qs} + \frac{\Delta}{2} \bar{\mathbf{K}}^{qs} \right) \bar{c}^{q-1s-1} - \frac{\Delta}{\tau} \bar{\mathbf{L}}^{qs} \sum_{p=1}^{s-1} (\bar{c}^{qp} - \bar{c}^{q-1p}). \end{aligned}$$

Clearly some initial status  $c(x)$  for  $t = 0$  and every  $x \in \Omega$  (here practically all  $c^{0s}$ ,  $s \in \{1, \dots, m\}$ ) must be given a priori. We can observe (understanding  $\bar{\mathbf{B}}^{0s}$ ,  $\bar{\mathbf{K}}^{0s}$  and  $\bar{F}^{0s}$  for  $c^{0s}$  in the same sense as  $\bar{\mathbf{B}}^{qs}$ ,  $\bar{\mathbf{K}}^{qs}$  and  $\bar{F}^{qs}$  for  $c^{qs}$ ) that if

$$\left( \mathbf{I} + \bar{\mathbf{B}}^{0s} + \frac{\Delta}{2} \bar{\mathbf{K}}^{0s} \right) \bar{c}^{0s} = \left( \mathbf{I} + \bar{\mathbf{B}}^{0s} - \frac{\Delta}{2} \bar{\mathbf{K}}^{0s} \right) \bar{c}^{0^{s-1}} + \bar{F}^{0s}$$

then  $c^{1s} = c^{0s}$  is a solution of our resulting equation with  $q = 1$ , etc. In other words: if an initial status is always stationary then no change of  $v$  and no time-redistribution of  $c$  can be expected. Of course all calculations must be done in all three phases; thus our mesh (uniform for formal simplicity here)  $\{0, \Delta, \dots, m\Delta\}$  has to cover  $\Omega$ ; outside  $I$  only some additive terms in the last formula degenerate to more simple ones.

**6. Conclusions.** We have derived a mathematical model of diffusional phase transformation that can simulate a lot of phenomena known from practical observations and measurements. For a stationary case we have developed a relatively robust and efficient solver, able to be applied to the sensitivity analysis of various changes of material characteristics (whose exact deterministic character is doubtful), including complicated “nonlinear corrections”  $\varphi_i$ , caused by non-trivial physical phenomena.

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To reach the higher level of understanding of diffusional phase transformation, the following research steps can be proposed: i) numerical simulations based on the non-stationary version of the presented solver, ii) development of the model for phase transformation of substitutional and interstitial (not purely substitutional) alloys, iii) including the generation and annihilation of vacancies (cf. [6]), connected with a significant deformation at the migrating interface. The results of simulations of transformation kinetics based on new models should be identified with dilatometric measurements for a selected set of alloys.

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