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THERMOMECHANICAL AND KINETIC APPROACHES TO DIFFUSIONAL–DISPLACIVE PHASE TRANSITIONS IN INELASTIC MATERIALS

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1. Introduction

Martensitic phase transformations (PT) are usually considered as diffusionless, i.e. solute atoms are frozen into the crystal lattice and do not redistribute during the transformation. If the temperature is high enough to allow diffusion during the PT time, redistribution of solute atoms can change the driving force, accelerate or suppress transformation of the crystal lattice or make it possible at all. Bainitic transformation and transformation from austenite to ferrite in steel belong to such diffusional-displacive PT. We do not know any continuum mechanical treatment of diffusional-displacive PT. In the physical literature [1–5] such transformations are studied as an interface propagation problem without consideration of stress and strain fields and continuum thermodynamics. The aim of this paper is an attempt to develop general continuum thermodynamic and kinetic approaches for diffusional-displacive PT. This approach will be based on the extension of a thermodynamic theory of martensitic PT and other structural changes in inelastic materials developed during the last few years [6–10].

2. General thermodynamic and kinetic theory

Thermodynamic relationships. Consider a volume V of multiphase material with a boundary S and given boundary conditions. Assume that in some volume V_n with a fixed boundary Σ_n relative to the material's points, due to diffusional–displacive PT during the time t_s the new nucleus of phase 2 appeared, i.e. some material mass m_n undergoes the PT. We will concentrate on the case with a sharp interface and local constitutive equations describing the deformation in each material point.

We will consider the simplest case of diffusion of one solute component with the mass fraction c in a solvent material. We assume an additive decomposition of a total strain tensor $\boldsymbol{\varepsilon}$ into elastic $\boldsymbol{\varepsilon}_e$, plastic $\boldsymbol{\varepsilon}_p$, thermal $\boldsymbol{\varepsilon}_\theta$ and transformational $\boldsymbol{\varepsilon}_t$ parts and misfit strain $\boldsymbol{\varepsilon}_c$, i.e.

$$\boldsymbol{\varepsilon} = \boldsymbol{\varepsilon}_e + \boldsymbol{\varepsilon}_p + \boldsymbol{\varepsilon}_\theta + \boldsymbol{\varepsilon}_t + \boldsymbol{\varepsilon}_c \,. \tag{1}$$

The transformation strain $\boldsymbol{\varepsilon}_t$ transforms a crystal lattice of the parent phase into a crystal lattice of the product phase. The misfit strain $\boldsymbol{\varepsilon}_c$ characterizes stress free deformation of a crystal lattice due to solute atoms. *The diffusional-displacive PT will be considered as a process of variation of the transformation strain and some or all thermomechanical properties from the initial to final value in an infinitesimal or finite transforming volume which is accompanied by a change in the fraction of solute atoms. Transformation process cannot be stopped at an intermediate state in any transforming point. The thermodynamic equilibrium for an intermediate value of the transformation strain or material properties is impossible.*

We introduce the internal dimensionless time (order parameter) ξ $(0 \leq \xi \leq 1)$, e.g. by formula $\xi := \frac{|\boldsymbol{\varepsilon}_t|}{|\boldsymbol{\varepsilon}_{t2}|}$, PT starts at $\xi = 0$ and finishes at $\xi = 1$; when ξ varies between 0 and 1, the transformation strain grows from $\boldsymbol{\varepsilon}_{t1}$ to $\boldsymbol{\varepsilon}_{t2}$, and all the thermodynamic properties of phase 1 change into the properties of phase 2. Note that the indices 1 and 2 denote the values before (for phase 1) and after (for phase 2) PT.

The misfit strain $\boldsymbol{\varepsilon}_c$ is assumed to be proportional to the change in the solute fraction during the diffusion, i.e. $\boldsymbol{\varepsilon}_c = \boldsymbol{b}(\xi)\,(c - c_1)$, $\boldsymbol{b}(0) = \boldsymbol{b}_1$, $\boldsymbol{b}(1) = \boldsymbol{b}_2$.

We will use an energy balance equation (the first law of thermodynamics) and the entropy balance equation combined with the Clausius-Duhem inequality (the second law of thermodynamics) for the whole volume V. As outside the nucleus V_n no PT occur and local constitutive equations are valid, both these equations can be rewritten for an arbitrary volume and for each material point without PT. Then the integral form of the first and the second laws of thermodynamics have to be used for the nucleus V_n only and will be accepted in the following form

$$\int\limits_{V_n} \left(\boldsymbol{\sigma} : \dot{\boldsymbol{\varepsilon}} - \rho \dot{U} - div\, \boldsymbol{h} + \rho r\right) dV_n - \frac{d}{dt} \int\limits_{\Sigma_n} \Gamma \, d\Sigma_n = 0 \,, \tag{2}$$

$$S_i := \frac{d}{dt} \int\limits_{V_n} \rho s \, dV_n - \int\limits_{V_n} \rho \frac{r}{\theta} \, dV_n + \int\limits_{\Sigma_n} \frac{\boldsymbol{h}}{\theta} \cdot \boldsymbol{n} \, d\Sigma_n - \int\limits_{\Sigma_n} \frac{\mu \boldsymbol{j}}{\theta} \cdot \boldsymbol{n} \, d\Sigma_n \geq 0 \,. \tag{3}$$

Here $\boldsymbol{\sigma}$ is the stress tensors, ρ is the mass density, U is the specific (per unit mass) internal energy, $\boldsymbol{h}$ the heat flux, r is the specific volumetric heat supply, t is the time, Γ is the surface energy per unit area after the PT, S_i is the total entropy production, s is the specific entropy, $\theta \geq 0$ is the temperature $\boldsymbol{n}$ is the unit normal to Σ_n, μ is the chemical potential of the solute component and $\boldsymbol{j}$ is the flux of solute atoms which satisfies the balance equation

$$\rho \dot{c} + div\, \boldsymbol{j} = 0 \,. \tag{4}$$

The energy balance equation (2) cannot be written for each material point due to the surface energy term, but the entropy inequality is valid for each point:

$$\tilde{S}_i := \rho \dot{s} - \rho \frac{r}{\theta} + \frac{1}{\theta} div\, \boldsymbol{h} - \frac{\nabla \theta}{\theta^2} \cdot \boldsymbol{h} - div \left(\frac{\mu \boldsymbol{j}}{\theta}\right) \geq 0 \,, \tag{5}$$

where $\tilde{S}_i$ is the local entropy production and transformation

$$\mathit{div}\,\frac{\boldsymbol{h}}{\theta} = \frac{1}{\theta}\,\mathit{div}\,\boldsymbol{h} + \boldsymbol{h}\cdot\nabla\left(\frac{1}{\theta}\right) = \frac{1}{\theta}\,\mathit{div}\,\boldsymbol{h} - \frac{1}{\theta^2}\,\boldsymbol{h}\cdot\nabla\theta \tag{6}$$

was used. Using the balance Eq.(4) we transform

$$\mathrm{div}\left(\frac{\mu\boldsymbol{j}}{\theta}\right) = \frac{\mu}{\theta}\,\mathrm{div}\,\boldsymbol{j} + \boldsymbol{j}\cdot\nabla\left(\frac{\mu}{\theta}\right) = -\frac{\rho\mu}{\theta}\,\dot{c} + \boldsymbol{j}\cdot\nabla\left(\frac{\mu}{\theta}\right). \tag{7}$$

Excluding the expression $\mathrm{div}\,\boldsymbol{h} - \rho r$ from Eq.(5) and substituting it in Eq.(2) we receive after evident transformations an inequality

$$\bar{\mathcal{D}} := \int\limits_{V_n} \rho\theta\tilde{S}_i\,dV_n = \int\limits_{V_n} \rho\mathcal{D}\,dV_n - \frac{d}{dt}\int\limits_{\Sigma_n} \Gamma\,d\Sigma_n \geq 0\,, \tag{8}$$

with

$$\begin{aligned}\rho\mathcal{D} &:= \boldsymbol{\sigma}:\dot{\boldsymbol{\varepsilon}} - \rho\dot{U} + \rho\theta\dot{s} - \frac{\nabla\theta}{\theta}\cdot\boldsymbol{h} + \rho\mu\dot{c} - \theta\boldsymbol{j}\cdot\nabla\left(\frac{\mu}{\theta}\right) = \\ &= \boldsymbol{\sigma}:\dot{\boldsymbol{\varepsilon}} - \rho\dot{\psi} - \rho s\dot{\theta} - \frac{\nabla\theta}{\theta}\cdot\boldsymbol{h} + \rho\mu\dot{c} - \theta\boldsymbol{j}\cdot\nabla\left(\frac{\mu}{\theta}\right)\end{aligned} \tag{9}$$

for the local rate of dissipation per unit volume and $\bar{\mathcal{D}}$ for the total dissipation rate; the specific Helmholtz free energy $\psi = U - \theta s$ is introduced.

Assume that $\psi = \psi(\boldsymbol{\varepsilon}_e\,, \theta\,, \boldsymbol{\varepsilon}_p\,, \boldsymbol{g}\,, \boldsymbol{\varepsilon}_t\,, c\,, \xi)$, where $\boldsymbol{g}$ is a set of internal variables, e.g. internal stress tensor (back stress), dislocations or point defect density. Substituting ψ and decomposition (1) in Eq.(9) we obtain

$$\begin{aligned}\mathcal{D} = \left(\frac{1}{\rho}\boldsymbol{\sigma} - \frac{\partial\psi}{\partial\boldsymbol{\varepsilon}_e}\right):\dot{\boldsymbol{\varepsilon}}_e - \left(s + \frac{\partial\psi}{\partial\theta} - \frac{\boldsymbol{\sigma}}{\rho}:\frac{\partial\boldsymbol{\varepsilon}_\theta}{\partial\theta}\right)\dot{\theta} + \boldsymbol{X}_p{:}\dot{\boldsymbol{\varepsilon}}_p + \boldsymbol{X}_g{:}\dot{\boldsymbol{g}} + \boldsymbol{X}_h{\cdot}\boldsymbol{h} + X_\xi\dot{\xi} + \\ \left(\mu + \frac{\boldsymbol{\sigma}}{\rho}:\frac{\partial(\boldsymbol{\varepsilon}_c + \boldsymbol{\varepsilon}_t + \boldsymbol{\varepsilon}_\theta)}{\partial c} - \frac{\partial\psi}{\partial c}\right)\dot{c} - \frac{\theta}{\rho}\,\boldsymbol{j}{\cdot}\nabla\left(\frac{\mu}{\theta}\right)\,,\end{aligned} \tag{10}$$

where

$$\boldsymbol{X}_p = \frac{1}{\rho}\boldsymbol{\sigma} - \frac{\partial\psi}{\partial\boldsymbol{\varepsilon}_p}; \qquad \boldsymbol{X}_g = -\frac{\partial\psi}{\partial\boldsymbol{g}^t}; \qquad \boldsymbol{X}_h = -\frac{1}{\rho}\frac{\nabla\theta}{\theta} \tag{11}$$

and

$$X_\xi = \frac{1}{\rho}\boldsymbol{\sigma}:\frac{\partial(\boldsymbol{\varepsilon}_t + \boldsymbol{\varepsilon}_\theta + \boldsymbol{\varepsilon}_c)}{\partial\xi} - \frac{\partial\psi}{\partial\boldsymbol{\varepsilon}_t}:\frac{\partial\boldsymbol{\varepsilon}_t}{\partial\xi} - \frac{\partial\psi}{\partial\xi} \tag{12}$$

are the dissipative forces conjugated to dissipative rates $\dot{\boldsymbol{\varepsilon}}_p$, $\dot{\boldsymbol{g}}$, $\boldsymbol{h}$ and $\dot{\xi}$ respectively. The assumption that the global rate of dissipation in Eq.(8) is independent of $\dot{\boldsymbol{\varepsilon}}_e$, $\dot{\theta}$ and $\dot{c}$ (which supposes that $\dot{c}$ does not change due to chemical reaction) results in the hyperelasticity law, expressions for the entropy and the chemical potential

$$\boldsymbol{\sigma} = \rho\frac{\partial\psi}{\partial\boldsymbol{\varepsilon}_e}\,; \qquad s = \frac{\boldsymbol{\sigma}}{\rho}:\frac{\partial\boldsymbol{\varepsilon}_\theta}{\partial\theta} - \frac{\partial\psi}{\partial\theta}\,; \tag{13}$$

$$\mu = -\frac{\boldsymbol{\sigma}}{\rho}:\frac{\partial(\boldsymbol{\varepsilon}_c + \boldsymbol{\varepsilon}_t + \boldsymbol{\varepsilon}_\theta)}{\partial c} + \frac{\partial\psi}{\partial c}\,. \tag{14}$$

For the global dissipation rate we have

$$\bar{\mathcal{D}} = \int\limits_{V_n} \rho\left(\boldsymbol{X}_p:\dot{\boldsymbol{\varepsilon}}_p + \boldsymbol{X}_g:\dot{\boldsymbol{g}} + \boldsymbol{X}_h\cdot\boldsymbol{h} + X_\xi\dot{\xi} - \frac{\theta}{\rho}\boldsymbol{j}\cdot\nabla\left(\frac{\mu}{\theta}\right)\right) dV_n - \dot{\Gamma} \geq 0\,. \qquad (15)$$

The simplest assumption that each rate $\dot{\boldsymbol{\varepsilon}}_p$, $\dot{\boldsymbol{g}}$, $\boldsymbol{h}$ and $\boldsymbol{j}$ depends locally on the conjugate force at the same material point only leads to evolution equations

$$\dot{\boldsymbol{\varepsilon}}_p = \boldsymbol{f}_p(\boldsymbol{X}_p, \xi)\,; \quad \dot{\boldsymbol{g}} = \boldsymbol{f}_g(\boldsymbol{X}_g, \xi)\,; \quad \boldsymbol{h} = \boldsymbol{f}_h(\boldsymbol{X}_h, \xi)\,; \quad \boldsymbol{j} = \boldsymbol{f}_j\left(\frac{\theta}{\rho}\nabla\left(\frac{\mu}{\theta}\right)\right), \qquad (16)$$

as well as to inequalities

$$\boldsymbol{X}_p:\dot{\boldsymbol{\varepsilon}}_p \geq 0\,, \qquad \boldsymbol{X}_g:\dot{\boldsymbol{g}} \geq 0\,, \qquad \boldsymbol{X}_h\cdot\boldsymbol{h} \geq 0\,, \qquad -\frac{\theta}{\rho}\boldsymbol{j}\cdot\nabla\left(\frac{\mu}{\theta}\right) \geq 0\,. \qquad (17)$$

The kinetic equation $\boldsymbol{j} = \boldsymbol{f}_j\left(\frac{\theta}{\rho}\nabla\left(\frac{\mu}{\theta}\right)\right)$ between the dissipative rate $\boldsymbol{j}$ and force $\frac{\theta}{\rho}\nabla\left(\frac{\mu}{\theta}\right)$ represents the generalized Fick's law and its substitution in balance Eq.(4) results in the diffusion equation

$$\rho\dot{c} = -div\left(\boldsymbol{f}_j\left(\frac{\theta}{\rho}\nabla\left(\frac{\mu}{\theta}\right)\right)\right)\,. \qquad (18)$$

Description of a phase transition. The assumption that PT is thermodynamically independent of all other thermodynamic processes, i.e. ξ is independent of $\boldsymbol{X}_p$, $\boldsymbol{X}_g$ and $\boldsymbol{X}_h$, leads to the inequality

$$\mathcal{D}_\xi := \int\limits_{V_n} \rho X_\xi\dot{\xi}\, dV_n - \dot{\Gamma} \geq 0\,. \qquad (19)$$

The above assumptions do not exclude a mutual influence of all thermomechanical processes through the stress and temperature fields. At $\dot{\Gamma} \neq 0$ inequality (19) cannot be localized; consequently PT have to be described by nonlocal equations.

Now let us show that even at $\dot{\Gamma} = 0$ we cannot prescribe for $\dot{\xi}$ a constitutive equation of type $\dot{\xi} = f_\xi(X_\xi, \xi)$ or any other constitutive equation. We assume that the condition $\dot{\xi} = 0$ can be satisfied with some external parameters, for example at $X_\xi = 0$. This is one scalar equation and it is always possible for each ξ and $\theta(\xi)$ to choose six components of stress tensor $\boldsymbol{\sigma}(\xi, \theta(\xi))$ to satisfy it, i.e. the phase equilibrium is possible for arbitrary ξ. According to our definition of PT, the phase equilibrium is impossible at $0 < \xi < 1$; only at $\xi = 0$ and $\xi = 1$ do we have the stable equilibrium. At $0 < \xi < 1$ a nonequilibrium process takes place, which requires energy and stress fluctuations.

Such a contradiction in the application of continuum thermodynamics was revealed for displacive PT in [7]. In this case a standard thermodynamic approach cannot be applied. It is necessary to average the thermodynamic parameters, related to PT, over the duration of PT t_s in order to filter off these fluctuations. We introduce the averaged dissipation rate due to PT

$$\bar{\mathcal{D}}_\xi := \frac{1}{t_s}\int\limits_0^{t_s} \mathcal{D}_\xi\, dt = \frac{1}{t_s}\left(\int\limits_{V_n}\int\limits_0^{t_s} \rho X_\xi\dot{\xi}\, dt\, dV_n - \int\limits_0^{t_s}\dot{\Gamma}\, dt\right) = \frac{X_v}{t_s} = X_v\dot{\chi}\,,$$

$$\text{where}\quad X_v := \int\limits_{V_n}\int\limits_0^1 \rho X_\xi \, d\xi \, dV_n - \Delta\bar{\Gamma}\,, \qquad \dot{\chi} := \frac{1}{t_s} \tag{20}$$

are the averaged dissipative force and rate, $\Delta\bar{\Gamma} := \bar{\Gamma}_2 - \bar{\Gamma}_1$.

For the driving force for PT using Eq.(12) we obtain

$$X_v = \int\limits_{V_n}\int\limits_{\boldsymbol{\varepsilon}_{t1}}^{\boldsymbol{\varepsilon}_{t2}} \rho\left(\frac{\boldsymbol{\sigma}}{\rho} - \frac{\partial\psi}{\partial\boldsymbol{\varepsilon}_t}\right) : d\boldsymbol{\varepsilon}_t \, dV_n + \int\limits_{V_n}\int\limits_0^1 \rho\left(\frac{\boldsymbol{\sigma}}{\rho} : \frac{\partial(\boldsymbol{\varepsilon}_\theta + \boldsymbol{\varepsilon}_c)}{\partial\xi} - \frac{\partial\psi}{\partial\xi}\right) d\xi \, dV_n - \Delta\bar{\Gamma}\,. \tag{21}$$

From Eqs.(9) and (10) it follows

$$\begin{aligned} X_\xi \dot{\xi} &= \mathcal{D} - \boldsymbol{X}_p : \dot{\boldsymbol{\varepsilon}}_p - \boldsymbol{X}_g : \dot{\boldsymbol{g}} - \boldsymbol{X}_h \cdot \boldsymbol{h} + \rho^{-1}\theta \boldsymbol{j} \cdot \boldsymbol{\nabla}\left(\frac{\mu}{\theta}\right) = \\ &= \rho^{-1}\boldsymbol{\sigma} : \dot{\boldsymbol{\varepsilon}} - \dot{\psi} - s\dot{\theta} - \boldsymbol{X}_p : \dot{\boldsymbol{\varepsilon}}_p - \boldsymbol{X}_g : \dot{\boldsymbol{g}} + \mu\dot{c}\,; \end{aligned} \tag{22}$$

$$X_v = \int\limits_{V_n}\left(\int\limits_{\boldsymbol{\varepsilon}_1}^{\boldsymbol{\varepsilon}_2} \boldsymbol{\sigma} : d\boldsymbol{\varepsilon} - \rho\Delta\psi - \int\limits_{\theta_1}^{\theta_2} \rho s \, d\theta - \int\limits_0^{t_s} \rho\left(\boldsymbol{X}_p : \dot{\boldsymbol{\varepsilon}}_p + \boldsymbol{X}_g : \dot{\boldsymbol{g}} + \mu\dot{c}\right) dt\right) dV_n - \Delta\bar{\Gamma}\,, \tag{23}$$

i.e. X_v is the dissipation increment due to PT only which is the difference between the total dissipation increment and the dissipation increment due to other dissipative processes (plastic flow, variation of internal variables and so on). Taking into account the decomposition (1) and Eq.(11)$_1$ for $\boldsymbol{X}_p$ we obtain

$$\begin{aligned} X_v &= \int\limits_{V_n}\left(\int\limits_{\boldsymbol{\varepsilon}_1}^{\boldsymbol{\varepsilon}_2} \boldsymbol{\sigma} : d(\boldsymbol{\varepsilon}_e + \boldsymbol{\varepsilon}_\theta + \boldsymbol{\varepsilon}_t + \boldsymbol{\varepsilon}_c) - \rho\,(\psi_2 - \psi_1) - \int\limits_{\theta_1}^{\theta_2} \rho s \, d\theta \, + \right. \\ &\left. + \int\limits_{\boldsymbol{g}_1}^{\boldsymbol{g}_2} \rho \frac{\partial\psi}{\partial\boldsymbol{g}^t} : d\boldsymbol{g} + \int\limits_{\boldsymbol{\varepsilon}_{p1}}^{\boldsymbol{\varepsilon}_{p2}} \rho \frac{\partial\psi}{\partial\boldsymbol{\varepsilon}_p} : d\boldsymbol{\varepsilon}_p + \int\limits_{c_1}^{c_2} \rho\mu \, dc\right) dV_n - \Delta\bar{\Gamma}\,. \end{aligned} \tag{24}$$

Kinetics. As is usual in irreversible thermodynamics, the kinetic equation between force and rate $\dot{\chi} = f(X_v, ...)$ or $X_v = K_v(\dot{\chi}, ...)$ has to be given. Functions f and K_v can depend on θ, $\boldsymbol{\varepsilon}_p$, $\boldsymbol{g}$, V_n, ... and should be determined experimentally. Sometimes it is convenient to present $K := \dfrac{K_v}{m_n} = \dfrac{1}{m_n}\displaystyle\int_{V_n} \rho\tilde{K} \, dV_n$, where $\tilde{K}$ is a locally determined function. Then introducing $\bar{X} := \frac{X_v}{m_n}$ we can express the kinetic equation in the form $\dot{\chi} = f\left(\bar{X} m_n, ...\right)$ or $\bar{X} = K(\dot{\chi}, ...)$. For homogeneously distributed $\tilde{K}$ we have $K = \tilde{K}$.

As an example of we consider size-dependent Arrhenius-type kinetic equation which includes both thermal activation and athermal threshold K^0:

$$\frac{1}{\dot{\chi}} = t_s = t_o \exp\left(-\frac{\left(\bar{X} - K^0 - E_a\right) m_n}{R\theta_{ef}} \frac{N}{n}\right) \qquad \text{at} \qquad 0 \le \bar{X} - K^0 \le E_a\,, \tag{25}$$

$$\dot{\chi} = 0 \qquad \text{at} \qquad \bar{X} - K^0 < 0\,. \tag{26}$$

Here E_a is the activation energy per unit mass at $\bar{X} - K^0 = 0$, $R = 8.314\ J/(K\ mol)$ is the gas constant, t_o is some characteristic time, $N = 6.02 \cdot 10^{23}$ is Avogadro's number (number of atoms in 1 *mol*). In Eq.(25) the actual activation energy includes difference $K^0 - \bar{X}$ to take into account the effect of the driving force, dissipative threshold and surface energy on kinetics. The lower bound for $\bar{X} - K^0$ in Eq.$(25)_2$ represents the PT criterion; the upper bound is due to the requirement of positiveness of an actual activation energy, since otherwise the process does not need thermal activation and Eq.(25) loses its sense. By introducing the effective temperature θ_{ef} we take into account the fact that temperature can vary significantly during the PT. As the simplest variant we define effective temperature as temperature averaged over the transformation process and transforming volume. The introduction in Eq.(25) of the number n of atoms in volume V_n which undergo thermal fluctuations allows us to consider transformation in a macroscopic volume in which multiple thermal fluctuations occur.

Extremum principle. The kinetic Eq.(25) is only one scalar equation which is not sufficient for the determination of all unknown parameters, e.g. position, shape, volume and orientation of nucleus and so on, which we will designate as $\boldsymbol{b}$. All functions in Eq.(25) depend on $\boldsymbol{b}$. To determine all actual parameters $\boldsymbol{b}$ among all admissible parameters $\boldsymbol{b}^*$ let us use the postulate of realizability [6–8]. We formulate the postulate of realizability in the following form:

as soon as PT can occur (i.e. when the PT criterion $\bar{X} \geq K^0$ is satisfied), it will occur during the time determined by equation (25) for each $\boldsymbol{b}^*$.

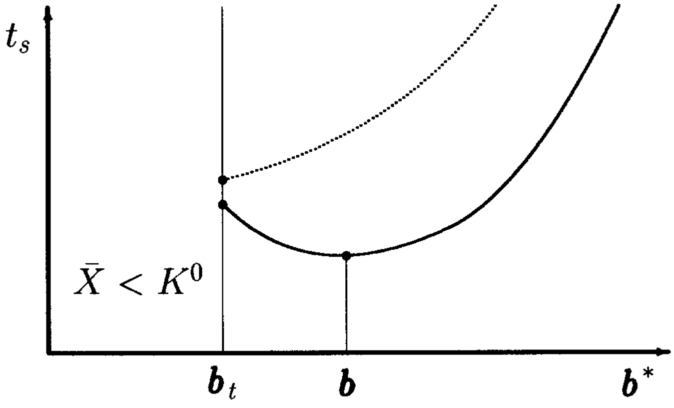

Fig. 1. Scheme for derivation of the principle of minimum of transformation time

Consequently, for each thermodynamically admissible parameter $\boldsymbol{b}^*$ PT can occur during the corresponding time, see Fig. 1. We are allowed to do nothing and simply wait. Then we will observe the PT which appears in the shortest time, i.e. we arrive at the *principle of minimum of transformation time*

$$t_s = t_o \exp - \frac{\left(\bar{X}(\boldsymbol{b}^*) - K^0(\boldsymbol{b}^*) - E_a(\boldsymbol{b}^*)\right) m_n^*}{R\,\theta_{ef}^*} \frac{N}{n} \longrightarrow min . \qquad (27)$$

Some specifications. Assume the validity of the following decomposition for the free energy

$$\rho\psi_i = 0.5\,\boldsymbol{\varepsilon}_e : \boldsymbol{E}_i : \boldsymbol{\varepsilon}_e + \rho\psi_i^\theta(\theta) + \rho\,\psi_i^c(c,\theta) = \rho\psi_i^e + \rho\,\psi_i^\theta(\theta) + \rho\psi_i^c(c,\theta)\ , \qquad i = 1, 2\ , \quad (28)$$

into elastic ψ_i^e, thermal ψ_i^θ parts and term ψ_i^c due to solute atoms, where $\boldsymbol{E}_i$ are constant (i.e. independent of strain, temperature and solute fraction) elastic moduli. For small strain approximation $\rho \simeq const$. We neglect the dependence of thermal constants on c. For ψ_i^θ known approximation (see e.g. [8]) can be used. In an approximation of the regular solution the following expression is valid [2, 11]

$$\rho\psi_i^c = \Omega_i^{-1}\left(e_{oi}c + k\theta(c \ln c + (1-c)\ln(1-c))\right) + 0.5\,u_{oi}c^2 . \tag{29}$$

Here Ω_i is the atomic volume of a solvent atom, k is the Boltzmann constant, constants e_{0i} and u_o characterize the self-energy and interaction energy of solute atoms.

Generally $\boldsymbol{\varepsilon}_\theta = \boldsymbol{\alpha}(\theta-\theta_o)$, where $\boldsymbol{\alpha} = \boldsymbol{\alpha}(\xi,\ \theta-\theta_o)$ is the thermal expansion tensor and θ_o is the reference temperature. We assume a linear approximation

$$\psi^\theta = (1-\xi)\,\psi_1^\theta + \xi\,\psi_2^\theta, \qquad \psi^c = (1-\xi)\,\psi_1^c + \xi\,\psi_2^c, \qquad \boldsymbol{b} = (1-\xi)\,\boldsymbol{b}_1 + \xi\,\boldsymbol{b}_2 . \tag{30}$$

$$\boldsymbol{E} = (1-\xi)\,\boldsymbol{E}_1 + \xi\,\boldsymbol{E}_2, \qquad \boldsymbol{\alpha} = (1-\xi)\,\boldsymbol{\alpha}_1 + \xi\,\boldsymbol{\alpha}_2 . \tag{31}$$

Then according to Eq.(12)

$$\begin{aligned} \rho X_\xi \;&=\; \boldsymbol{\sigma}:\frac{\partial \boldsymbol{\varepsilon}_t}{\partial \xi} + \boldsymbol{\sigma}:\Delta\boldsymbol{\alpha}\,(\theta-\theta_o) + \boldsymbol{\sigma}:\Delta\boldsymbol{b}\,(c-c_1) - 0.5\,\boldsymbol{\varepsilon}_e:\Delta\boldsymbol{E}:\boldsymbol{\varepsilon}_e - \\ &-\; \rho\Delta\psi^\theta(\theta) - \rho\Delta\psi^c(c,\theta)\ ; \end{aligned} \tag{32}$$

$$\begin{aligned} \rho X \;&:=\; \int_0^1 \rho X_\xi\, d\xi = \int_{\boldsymbol{\varepsilon}_{t1}}^{\boldsymbol{\varepsilon}_{t2}} \boldsymbol{\sigma}:d\boldsymbol{\varepsilon}_t + \int_0^1 \boldsymbol{\sigma}:\Delta\boldsymbol{\alpha}\,(\theta-\theta_o)\, d\xi + \int_0^1 \boldsymbol{\sigma}:\Delta\boldsymbol{b}\,(c-c_1)\, d\xi - \\ &-\; 0.5\int_0^1 \boldsymbol{\varepsilon}_e:\Delta\boldsymbol{E}:\boldsymbol{\varepsilon}_e\, d\xi - \int_0^1 \left(\rho\Delta\psi^\theta(\theta) + \rho\Delta\psi^c(c,\,\theta)\right) d\xi . \end{aligned} \tag{33}$$

It is important to mention that the change in free energy due to diffusion affects the PT only when there is a difference between free energy parts $\Delta\psi^c$ related to solute atoms. The misfit strain affects PT in two ways: first, due to the third term in Eq.(33) proportional to the change in misfit strain during the PT; second, even at $\Delta\boldsymbol{b} = 0$ misfit strain changes the stress distribution and contributes to the first, second and fourth terms in Eq.(33). If ψ_i^c and $\boldsymbol{b}_i$ are the same for both phases and the stress variation due to misfit strain is negligible, diffusion does not change the driving force for PT, because the change in free energy due to diffusion and work $\boldsymbol{\sigma}:d\boldsymbol{\varepsilon}_c$ in Eq.(23) is completely compensated for by the term $\mu\, dc$.

The solute volume fraction c and temperature variation during the PT are determined by the solution of coupled temperature evolution and diffusion equations. If we assume for simplicity $c - c_1 = \Delta c\,\xi$ and an isothermal process at $\theta = \theta_o$ then Eq.(33) transforms into

$$\begin{aligned} \rho X \;&=\; \int_{\boldsymbol{\varepsilon}_{t1}}^{\boldsymbol{\varepsilon}_{t2}} \boldsymbol{\sigma}:d\boldsymbol{\varepsilon}_t + \int_0^1 \boldsymbol{\sigma}:\Delta\boldsymbol{b}\,\Delta c\,\xi\, d\xi - 0.5\int_0^1 \boldsymbol{\varepsilon}_e:\Delta\boldsymbol{E}:\boldsymbol{\varepsilon}_e\, d\xi - \\ &-\; \rho\Delta\psi^\theta(\theta_o) - f(c_2,\, c_1,\, \theta_o)\ , \end{aligned} \tag{34}$$

where

$$f(c_2,\, c_1,\, \theta_o) := \Delta c^{-1}\int_{c_1}^{c_2} \rho\Delta\psi^c(c,\, \theta_o)\, dc = \tag{35}$$

$$\begin{aligned}
&= 0.5\,\Delta c^{-1}\Big[\Delta\left(\Omega^{-1} e_o\right)\left(c_2^2 - c_1^2\right) + \frac{1}{3}\,\Delta u_o\left(c_2^3 - c_1^3\right) + \\
&+ \Delta\Omega^{-1} k\,\theta_o\Big(c_2^2\ \ln c_2 - c_1^2\ \ln c_1 - \frac{1}{2}\left(c_2^2 - c_1^2\right) + \\
&+ (1 - c_2)^2 \ln(1 - c_2) - (1 - c_1)^2 \ln(1 - c_1) - \frac{1}{2}\left((1 - c_2)^2 - (1 - c_1)^2\right)\Big)\Big]\,.
\end{aligned}$$

When the volumetric transformation strain is zero, then $\Delta\Omega^{-1} = 0$ and the first two terms in Eq.(35) remain only. At small c or Δc the second term can be neglected as well.
Temperature evolution. Generally it is impossible to obtain the local temperature evolution equation due to the term with surface energy. If we will neglect the surface energy in dissipation inequality (8), then $\theta\tilde{S}_i = \mathcal{D}$ and the combination of this relation with the local entropy production equation (5) results in an entropy balance equation

$$\rho\,\theta\,\dot{s} = \rho\mathcal{D} - div\,\boldsymbol{h} + \frac{\boldsymbol{\nabla}\theta}{\theta}\cdot\boldsymbol{h} - \rho\,\mu\,\dot{c}\,. \tag{36}$$

Substitution of an expression for the local rate of dissipation from Eq.(15) in Eq.(36) yields

$$\theta\,\dot{s} = -\rho^{-1}\,div\,\boldsymbol{h} + \boldsymbol{X}_p{:}\dot{\boldsymbol{\varepsilon}}_p + \boldsymbol{X}_g{:}\dot{\boldsymbol{g}} + X_\xi\,\dot{\xi} - \mu\,\dot{c}\,. \tag{37}$$

As $s = s\,(\theta,\,\boldsymbol{\sigma},\,\boldsymbol{g},\,\boldsymbol{\varepsilon}_p,\,c,\,\xi)$ (see Eq.(13)), then substitution of this expression and generalized Fourier law $\boldsymbol{h} = \boldsymbol{f}_h\left(-\frac{\boldsymbol{\nabla}\theta}{\theta}\right)$ into Eq.(37) leads to the temperature evolution equation

$$\begin{aligned}
\nu\,\dot{\theta} &= -\rho^{-1}\,div\,\boldsymbol{f}_h\left(-\frac{\boldsymbol{\nabla}\theta}{\theta}\right) + \left(\boldsymbol{X}_p - \frac{\partial s}{\partial\boldsymbol{\varepsilon}_p}\,\theta\right):\dot{\boldsymbol{\varepsilon}}_p + \left(\boldsymbol{X}_g - \frac{\partial s}{\partial\boldsymbol{g}}\,\theta\right):\dot{\boldsymbol{g}} + \\
&+ \left(X_\xi - \frac{\partial s}{\partial\xi}\,\theta\right)\dot{\xi} - \theta\,\frac{\partial s}{\partial\boldsymbol{\sigma}}:\dot{\boldsymbol{\sigma}} - \left(\mu + \frac{\partial s}{\partial c}\,\theta\right)\dot{c}\,, \qquad \nu := \theta\,\frac{\partial s}{\partial\theta}\,,
\end{aligned} \tag{38}$$

where ν is the specific heat at constant $\boldsymbol{\sigma}$, $\boldsymbol{g}$, $\boldsymbol{\varepsilon}_p$, ξ and c. For the *adiabatic* process, i.e. at $\mathrm{div}\,\boldsymbol{h} = 0$, when Eq.(38) determines the temperature evolution in each material point independently, i.e. without a solution of the boundary-value problem.

3. Appearance of a spherical nucleus

As the simplest example we consider the nucleation of a spherical particle with the radius r in an infinite elastic-perfectly plastic sphere under applied external pressure at diffusional-displacive PT. Let the transformation strain $\boldsymbol{\varepsilon}_t = \frac{1}{3}\varepsilon_0\,\xi\,\boldsymbol{I}$ and the misfit strain $\boldsymbol{\varepsilon}_c = \frac{1}{3}\varepsilon_c\,\boldsymbol{I}$ be purely dilatational, where $\varepsilon_0\,\xi$ and ε_c are the volumetric transformation and misfit strain, $\boldsymbol{I}$ the unit tensor, i.e. $\varepsilon_c = b(\xi)\,(c - c_1) = b(\xi)\,\Delta c\,\xi = b_1\,\Delta c\,\xi + \Delta b\,\Delta c\,\xi^2$. We assume that solute atoms are homogeneously distributed in the nucleus. Approximating the quadratic with respect to the ξ term in ε_c with the linear one, i.e. $\Delta b\,\Delta c\,\xi^2 \approx 0.5\,\Delta b\,\Delta c\,\xi$, we obtain

$$\boldsymbol{\varepsilon}_t + \boldsymbol{\varepsilon}_c = \frac{1}{3}\left(\varepsilon_o + 0.5\,(b_1 + b_2)\,\Delta c\right)\xi\,\boldsymbol{I} := \frac{1}{3}\varepsilon_{tc}\,\xi\,\boldsymbol{I}\,. \tag{39}$$

Now we can use equations for stress variation from paper [6], in which transformation strain ε_o has to be replaced with ε_{tc}. Then

$$\int_{\boldsymbol{\varepsilon}_{t1}}^{\boldsymbol{\varepsilon}_{t2}} \boldsymbol{\sigma} : d\boldsymbol{\varepsilon}_t + 0.5 \int_0^1 \boldsymbol{\sigma} : \Delta \boldsymbol{b} \Delta c \, d\xi =$$

$$\int_0^1 p(\varepsilon_{tc}\xi) d(\varepsilon_0 \xi) + 0.5 \int_0^1 p(\varepsilon_{tc}\xi) \Delta b \Delta c \, d\xi = \int_0^1 p(\varepsilon_{tc}\xi) d(\varepsilon_{tc}\xi) \left(1 - \tfrac{b_1 \Delta c}{\varepsilon_{tc}}\right).$$

Calculating the last integral in the same way as in paper [6] with ε_{tc} instead of ε_0, we obtain for X

$$\rho X = \left(p\varepsilon_{tc} - \frac{2}{3}\sigma_y \left(\sigma_y C + \dot{\varepsilon}_{tc} \ln \frac{\varepsilon_{tc}}{2\sigma_y C}\right)\right) \left(1 - \frac{b_1 \Delta c}{\varepsilon_{tc}}\right) - \rho \Delta \psi^\theta(\theta_o) - f(c_2, c_1) \, . \quad (40)$$

As c_1 before PT in the parent phase is known, Eq.(25) contains three unknowns: r, c_2 and t_s. The following relation

$$r_d^2 = 2D \frac{c_1 - c_{1r}}{c_2 - c_{1r}} t \, , \quad (41)$$

is the consequence of the solution of the diffusion equation, where D is the diffusion coefficient, t is the diffusion time and c_{1r} is the solute volume fraction in the parent phase at the interface [2, 11]. This equation determines the radius r_d of a sphere in which during the time t the volume fraction c_2 can be reached. Additionally, the constraint

$$c_{min} \leq c_2 \leq c_{max} \quad (42)$$

must be taken into account. It means, in particular, that the fraction of solute cannot exceed some possible maximum value, determined by the type of crystal lattice and the difference in atomic size of solute and solvent atoms. The minimum value can be zero or determined from the thermodynamic condition for solute atoms across the interface. For example, if the solute has a very high mobility, the equality of the solute chemical potential in phase 1 and phase 2 can be assumed which relates c_2 and c_{1r}.

If during time t the nucleus with the radius r with the volume fraction c_2 of solute atoms appears, then the inequality

$$r \leq r_d = \left(2D \frac{c_1 - c_{1r}}{c_2 - c_{1r}} t\right)^{0.5} \quad (43)$$

has to be valid. In the opposite case the fraction c_2 cannot be reached in the nucleus with radius r during the nucleation time. If $r < r_d$, then diffusion can guarantee fraction c_2 during the nucleation time in the sphere larger than the nucleus, i.e. diffusion does not limit the transformation kinetics. This can take place for example when $c_2 = c_{max} > c_1$ or $c_2 = c_{min} < c_1$, i.e. when the solute volume fraction in the nucleus reaches the maximum or minimum possible values. Consequently, if the solution obtained satisfies the inequality $r < r_d$, then the process is transformation controlled and we do not need Eq.(41); in the case $r = r_d$ the kinetics is diffusion controlled.

To illustrate the approach only, we assume for simplicity that c_{1r} is known from the solution of the diffusion equation and is independent of c_2; temperature is fixed. Let us consider the following cases.

Let diffusion be a limiting process, i.e. $r = r_d$ and constraint (42) is satisfied. Finding c_2 from Eq.(41)

$$c_2 = 2D(c_1 - c_{1r})\frac{t}{r^2} + c_{1r}\,, \tag{44}$$

substituting this c_2 in X (and probably in K^0 and E_a) and minimizing transformation time according to principle (27), we derive an additional equation

$$-\frac{\partial(X - K^0 - E_a)}{\partial c_2}\,\frac{4D(c_1 - c_{1r})\rho t}{3} + \left(X - K^0 - E_a\right)\rho r^2 - 2\Gamma r = 0\,. \tag{45}$$

Eqs.(25) and (45) after substitution of expression (44) for c_2 in them represent two equations with respect to two unknowns r and t. After substitution of t from Eq.(45) into Eq.(25), we get the nonlinear algebraic equation to find r. It is assumed that $\bar{X} \geq K^0$.

Let us analyze the results obtained.

1. In the case without diffusion ($D = 0$ or when X, K^0 and E_a do not depend on c_2) the first term in Eq.(45) is zero, this equation has no positive solution (as $(X - K^0 - E_a) < 0$) and we arrive at the same situation as for pore nucleation [8], i.e. $r \rightarrow min$ and r is determined from the thermodynamic PT criterion $\bar{X} = K^0$, i.e.

$$\left(X - K^0\right)\frac{4}{3}\pi r_t^3\rho - \Gamma 4\pi r_t^2 = 0 \qquad \text{or} \qquad r_t = \frac{3\Gamma}{\rho(X - K^0)}\,. \tag{46}$$

A nucleus (void) with a radius r_t is called the *thermodynamically admissible nucleus* [8]. Relation between thermodynamically admissible and critical nucleus is analyzed in [8]. Substitution of condition $\bar{X} = K^0$ in Eq.(25) results in

$$t_s = t_o \exp\left(\frac{\rho E_a}{R\theta_{ef}}\,\frac{N}{n}\,\frac{4}{3}\pi r_t^3\right)\,. \tag{47}$$

If diffusion promotes the PT and increases the difference $X - K^0 - E_a$, i.e. the first term $\dfrac{\partial(X - K^0 - E_a)}{\partial r}$ in Eq.(45) is negative, then again this equation has no positive roots. In this case $r \rightarrow min$, the PT criterion (46), the kinetic equation (47) and diffusion Eq.(44) are three equations for the determination of three unknowns r, c_2 and t. Substituting t from Eq.(44) in kinetic equation (47), and then r from Eq.(46) in Eq.(47), we obtain a nonlinear equation with respect to c_2. Substituting c_2 found in Eq.(46) we can find r, and then t from Eq.(44). Then we have to check inequality (42).

2. If diffusion suppresses the PT and decreases the difference $X - K^0 - E_a$, i.e. the first term $\dfrac{\partial(X - K^0 - E_a)}{\partial r}$ in Eq.(45) is positive, then a solution of Eq.(45) for "optimal" r exists. If it exceeds the thermodynamically admissible radius and inequality (42) is in fact satisfied, then it is the actual solution.

3. Let the solution obtained not satisfy the thermodynamic PT criterion (46), i.e. $r < r_t$. Then we should repeat the same procedure as in item 1.

4. Let one of the inequalities (42) be violated, e.g. $c > c_{max}$. Then we put $c = c_{max}$ and substitute it in kinetic Eq.(25). As in this case X is independent of r, the principle of the minimum of transformation time reduces to the $r \rightarrow min$ and the minimum value of r is determined from the PT criterion (46), and the transformation time can be found from kinetic equation (47). If $r \leq r_d$, then we have obtained the actual solution.

5. Let us obtain for the case $c = c_{max}$ considered in item 4 $r > r_d$, i.e. diffusion is a limiting process. Then we put $r = r_d$ and two Eqs.(25) and (44) determine two unknowns r and t and an additional extremum principle is not necessary. If r satisfies PT criterion $\bar{X} \geq K^0$, then the solution obtained is the actual one. In the opposite case, a solution does not exist.

4. Concluding remarks

A suggested theory of diffusional–displacive PT in inelastic materials is an extension of the theory of martensitic PT and other structural changes developed in [4–11]. That is why it is easy to take large deformations and displacement discontinuity into account in the same way as in [6, 7]. Interface propagation condition can be derived by considering the PT in the infinitesimal volume covered by moving interface [6–8, 10]. Generalization for diffusion of n types of solute atoms, as well as for for chemically reacting solute substances is straightforward. Effect of stresses on diffusion is taken into account. However, due to defect generation, plastic deformation may affect the diffusion significantly which has to be incorporated in model. Coupling of stress, temperature and solute fraction fields may be of great importance as well.

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