



THERMOMECHANICS AND KINETICS OF GENERALIZED SECOND-ORDER PHASE TRANSITIONS IN INELASTIC MATERIALS. APPLICATION TO DUCTILE FRACTURE

Valery I. Levitas

University of Hannover, Institute for Structural and Computational Mechanics,
Appelstraße 9A, 30167 Hannover, Germany

(Received 26 February 1998; accepted for print 9 April 1998)

1. Introduction

According to the classical definition [1], for first-order phase transformations (FOPT) in liquids or gases the thermodynamic Gibbs potential $G(p, \theta)$ is continuous along the phase equilibrium line $\theta_e(p_e)$ in the $\theta - p$ plane, but its first and higher derivatives have jumps. Here θ and p are the temperature and pressure respectively. For second-order phase transformations (SOPT), the thermodynamic potential and its first derivatives are continuous along the phase equilibrium line $\theta_e(p_e)$, but its second derivatives have jumps. Temperature and pressure are equal for both phases and are considered as independent parameters. It is clear that the SOPT can be treated as a particular case of the FOPT. In particular, the well-known Clausius-Clapeyron relation derived for the FOPT can be transformed into Ehrenfest equation for the SOPT.

Generalization of the definition of SOPT and Ehrenfest equation for nonlinear elastic solids is given in [2]. According to [2], the SOPT surface is determined in a space of strain tensor $\boldsymbol{\varepsilon}$ and temperature at which the Helmholtz free energy $\psi(\boldsymbol{\varepsilon}, \theta) = G + \boldsymbol{\sigma}:\boldsymbol{\varepsilon}$ and its first derivatives (stress tensor $\boldsymbol{\sigma}$ and entropy s) are continuous, but the second derivatives have jumps. For such SOPT, formulation in terms of Helmholtz and Gibbs free energy is equivalent due to the continuity of $\boldsymbol{\sigma}$ and $\boldsymbol{\varepsilon}$. The main problem is related to the fact that with such a definition the SOPT cannot be considered as a particular case of the FOPT, according to their modern definitions [3-5]. For FOPT in elastic materials, the phase transformation (PT) condition is determined not for each material point in $\boldsymbol{\sigma} - \theta$ or $\boldsymbol{\varepsilon} - \theta$ space, but for points of the interface between two phases [3]. Only three components of the stress tensor are continuous across the interface and, as the strain tensor has jump across the interface as well, it is impossible to formulate a PT condition for each material point in $\boldsymbol{\sigma} - \theta$ or $\boldsymbol{\varepsilon} - \theta$ space without solving a boundary-value problem. In the adiabatic case the temperature is also discontinuous. For PT in elastic materials with hysteresis due to interface friction, the Gibbs potential has a jump across an interface as well [4, 5].

For elastoplastic materials the situation is much more complicated, because a thermomechanical process in some volume has to be considered and not only the jump, but the path-dependent

variation of all the parameters determines the PT conditions [4].

Consequently, the definition of SOPT given in [2] selects a very narrow class of phenomena in comparison with those for the FOPT. The aim of this paper is to define and study SOPT in inelastic solids, which are considered as a *particular case of the FOPT* treated in [4]. We will call them *generalized SOPT*. The necessity of such a study is evident: some PT (e.g. ferroelectric and ferromagnetic) are considered as SOPT, but *more precisely as FOPT with a small transformation strain and jump in entropy* [1, 6]. The PT conditions and extremum principle for the determination of all unknown parameters for *generalized SOPT* will be derived. These considerations include as a particular case fracture, which allows us to derive a new fracture criterion and extremum principle.

2. Thermodynamics of generalized second-order phase transitions

Definition of generalized SOPT. For the reasons mentioned in the Introduction, it is impossible to use for solids the classical definition of the FOPT for liquids, because in the general case neither the Gibbs potential, nor its arguments (stress and temperature) are fixed during the FOPT. That is why before giving a definition for the generalized SOPT we have to formulate a problem for the FOPT in a proper form. For FOPT the Helmholtz free energy of each phase $\psi_1(\boldsymbol{\varepsilon}_{e1}, \theta_1, \boldsymbol{\varepsilon}_{p1}, \mathbf{g}_1)$ and $\psi_2(\boldsymbol{\varepsilon}_{e2}, \theta_2, \boldsymbol{\varepsilon}_{p2}, \mathbf{g}_2)$ has to be given (determined experimentally). Here $\boldsymbol{\varepsilon}_e$ and $\boldsymbol{\varepsilon}_p$ are the elastic and plastic strains, \mathbf{g} is a set of internal variables and the indices 1 and 2 denote the values before PT (in phase 1) and after PT (in phase 2). Additionally, the transformation strain $\boldsymbol{\varepsilon}_t$, which transforms a crystal lattice of the parent phase into a crystal lattice of the product phase, is introduced in an additive decomposition of a total strain tensor $\boldsymbol{\varepsilon} = \boldsymbol{\varepsilon}_e + \boldsymbol{\varepsilon}_p + \boldsymbol{\varepsilon}_\theta + \boldsymbol{\varepsilon}_t$, where $\boldsymbol{\varepsilon}_\theta$ is the thermal strain. Consider a volume V of material in phase 1 with a boundary S and prescribed boundary and initial conditions. It is necessary to describe the process of emergence and change of the second phase with the change of boundary conditions.

In order to develop a similar formulation for SOPT, we have to find the counterparts of the condition of continuity of volume (strain) and entropy. As one of these conditions we can adopt the absence of transformation strain $\boldsymbol{\varepsilon}_t = \mathbf{0}$. In order to formulate the second condition, let us introduce for FOPT the transformation entropy s_t in the following way. We define the equilibrium temperature of phases θ_e at $\boldsymbol{\varepsilon}_{ei} = \boldsymbol{\varepsilon}_{pi} = \mathbf{g}_i = \mathbf{0}$, $i = 1, 2$, (consequently $\boldsymbol{\sigma}_i = \mathbf{0}$) form condition $\psi_1(\mathbf{0}, \theta_e, \mathbf{0}, \mathbf{0}) = \psi_2(\mathbf{0}, \theta_e, \mathbf{0}, \mathbf{0})$. Then we introduce by definition transformation entropy at $\boldsymbol{\varepsilon}_{ei} = \boldsymbol{\varepsilon}_{pi} = \mathbf{g}_i = \mathbf{0}$, $i = 1, 2$, as $s_t := s_2(\mathbf{0}, \theta_e, \mathbf{0}, \mathbf{0}) - s_1(\mathbf{0}, \theta_e, \mathbf{0}, \mathbf{0})$. By definition, for generalized SOPT $s_t = 0$.

Let us give a definition. *Generalized SOPT is a thermomechanical process of change in the thermomechanical properties of materials (elastic moduli \mathbf{E} , heat capacity ν , thermal expansion coefficient $\boldsymbol{\alpha}$, yield condition, hardening rules and so on) from initial to final values in some region (e.g. in a nucleus or volume covered by a moving interface) at zero transformation strain $\boldsymbol{\varepsilon}_t = \mathbf{0}$ and transformation entropy $s_t = 0$. This process cannot be stopped at material point in the intermediate state.*

Introduction of an order parameter. Let us consider a uniformly deformed infinitesimal region (material point) in a process of SOPT. For SOPT a kinematic decomposition reduces to the form

$$\boldsymbol{\varepsilon} = \boldsymbol{\varepsilon}_e + \boldsymbol{\varepsilon}_p + \boldsymbol{\varepsilon}_\theta. \quad (1)$$

We introduce the order parameter (internal dimensionless time) ξ ($0 \leq \xi \leq 1$) which is related to all the variable parameters (\mathbf{E} , ν , $\boldsymbol{\varepsilon}_\theta$) and has the following properties: PT starts at $\xi = 0$ and finishes at $\xi = 1$; when ξ varies between 0 and 1, the parameters \mathbf{E} , ν and $\boldsymbol{\varepsilon}_\theta$ vary from \mathbf{E}_1 , ν_1 , $\boldsymbol{\varepsilon}_{\theta 1}$ to \mathbf{E}_2 , ν_2 , $\boldsymbol{\varepsilon}_{\theta 2}$. It is possible to define

$$\xi := \frac{1}{3} \left(\frac{|\mathbf{E} - \mathbf{E}_1|}{|\mathbf{E}_2 - \mathbf{E}_1|} + \frac{\nu - \nu_1}{\nu_2 - \nu_1} + \frac{|\boldsymbol{\varepsilon}_\theta - \boldsymbol{\varepsilon}_{\theta 1}|}{|\boldsymbol{\varepsilon}_{\theta 2} - \boldsymbol{\varepsilon}_{\theta 1}|} \right), \quad (2)$$

a lot of other definitions are acceptable. Important point is, that all variable parameters have to be included in the definition of ξ . In the opposite case ξ can reach 1 before e.g. ϵ_θ reaches $\epsilon_{\theta 2}$ and PT finishes. The specific Helmholtz free energy $\psi = \psi(\epsilon_e, \theta, \epsilon_p, \mathbf{g}, \xi)$, at $\xi = 0$ and $\xi = 1$ coincides with ψ_1 and ψ_2 respectively. We admit the second law of thermodynamic in the form of the Clausius-Duhem inequality

$$\mathcal{D} = \boldsymbol{\sigma} : \dot{\boldsymbol{\epsilon}} - \rho \dot{\psi} - \rho s \dot{\theta} - \frac{\nabla \theta}{\theta} \cdot \mathbf{h} \geq 0. \quad (3)$$

Here \mathcal{D} is the rate of dissipation per unit volume, ρ the mass density at $\xi = 0$, $\nabla \theta$ the temperature gradient, \mathbf{h} the heat flux. The substitution of the rate of free energy in Eq.(3) with taking into account the additive decomposition of $\boldsymbol{\epsilon}$ and $\dot{\boldsymbol{\epsilon}}_\theta = \frac{\partial \boldsymbol{\epsilon}_\theta}{\partial \theta} \dot{\theta} + \frac{\partial \boldsymbol{\epsilon}_\theta}{\partial \xi} \dot{\xi}$ yields

$$\begin{aligned} \mathcal{D} = & \left(\boldsymbol{\sigma} - \rho \frac{\partial \psi}{\partial \boldsymbol{\epsilon}_e} \right) : \dot{\boldsymbol{\epsilon}}_e - \rho \left(s + \frac{\partial \psi}{\partial \theta} - \frac{\boldsymbol{\sigma}}{\rho} : \frac{\partial \boldsymbol{\epsilon}_\theta}{\partial \theta} \right) \dot{\theta} + \\ & + \left(\boldsymbol{\sigma} - \rho \frac{\partial \psi}{\partial \boldsymbol{\epsilon}_p} \right) : \dot{\boldsymbol{\epsilon}}_p - \rho \frac{\partial \psi}{\partial \mathbf{g}^t} : \dot{\mathbf{g}} - \frac{\nabla \theta}{\theta} \cdot \mathbf{h} + \left(\boldsymbol{\sigma} : \frac{\partial \boldsymbol{\epsilon}_\theta}{\partial \xi} - \rho \frac{\partial \psi}{\partial \xi} \right) \dot{\xi} \geq 0. \end{aligned} \quad (4)$$

Here a superscript t denote transposition, dots mean contractions of the tensors.

The assumption that the rate of dissipation is independent of $\dot{\boldsymbol{\epsilon}}_e$ and $\dot{\theta}$ results in the hyperelasticity law and expression for entropy, as well as in a reduced dissipative inequality:

$$\boldsymbol{\sigma} = \rho \frac{\partial \psi}{\partial \boldsymbol{\epsilon}_e}; \quad s = \frac{\boldsymbol{\sigma}}{\rho} : \frac{\partial \boldsymbol{\epsilon}_\theta}{\partial \theta} - \frac{\partial \psi}{\partial \theta}; \quad (5)$$

$$\mathcal{D} = \mathbf{X}_p : \dot{\boldsymbol{\epsilon}}_p + \mathbf{X}_g : \dot{\mathbf{g}} + \mathbf{X}_h \cdot \mathbf{h} + X_\xi \dot{\xi} \geq 0, \quad (6)$$

$$\text{where } \mathbf{X}_p = \boldsymbol{\sigma} - \rho \frac{\partial \psi}{\partial \boldsymbol{\epsilon}_p}; \quad \mathbf{X}_g = -\rho \frac{\partial \psi}{\partial \mathbf{g}^t}; \quad \mathbf{X}_h = -\frac{\nabla \theta}{\theta} \quad \text{and} \quad (7)$$

$$X_\xi = \boldsymbol{\sigma} : \frac{\partial \boldsymbol{\epsilon}_\theta}{\partial \xi} - \rho \frac{\partial \psi}{\partial \xi} \quad (8)$$

are the dissipative forces conjugated to dissipative rates $\dot{\boldsymbol{\epsilon}}_p$, $\dot{\mathbf{g}}$, \mathbf{h} and $\dot{\xi}$ respectively. The simplest assumption that each rate depends on the conjugate force only leads to evolution equations

$$\dot{\boldsymbol{\epsilon}}_p = \mathbf{f}_p(\mathbf{X}_p, \xi); \quad \dot{\mathbf{g}} = \mathbf{f}_g(\mathbf{X}_g, \xi); \quad \mathbf{h} = \mathbf{f}_h(\mathbf{X}_h, \xi); \quad \dot{\xi} = f_\xi(X_\xi, \xi). \quad (9)$$

Eq.(9)₁ is the flow rule, Eq.(9)₂ is the evolution equation for the internal variables, Eq.(9)₃ is the generalized Fourier law and Eq.(9)₄ is the kinetic equation for PT. We consider the last equation for the description of PT only.

Averaging over the PT time. We assume that the condition $\dot{\xi} = 0$ is valid at $X_\xi = 0$ only. i.e. the equation $X_\xi = 0$ describes the equilibrium PT. This equation allows to determine the equilibrium stress variation $\boldsymbol{\sigma}(\xi)$ in the course of PT. If the actual stress variation follows this dependence, then transformation can be stopped at arbitrary ξ , which contradicts to our definition of SOPT. We see that a standard thermodynamical approach cannot be applied. As for FOPT, it is necessary to average the thermodynamical parameters, related to PT, over the transformation time t_p . We introduce the averaged dissipation rate due to the PT

$$\mathcal{D}_\xi := \frac{1}{t_p} \int_0^{t_p} X_\xi \dot{\xi} dt = \frac{1}{t_p} \int_0^1 X_\xi d\xi = \frac{X}{t_p} = X \dot{\chi}, \quad \text{where } X := \int_0^1 X_\xi d\xi, \quad \dot{\chi} := \frac{1}{t_p} \quad (10)$$

are the averaged dissipative force and rate. The definition of dissipative rate is logical, because a variation of the parameter ξ during the time t_p is one. The dissipative force is defined as a

conjugate variable in the expression for the rate of dissipation. From Eqs.(3) and (6) it follows

$$X_\xi \dot{\xi} = \mathcal{D} - \mathbf{X}_p : \dot{\boldsymbol{\varepsilon}}_p - \mathbf{X}_g : \dot{\mathbf{g}} - \mathbf{X}_h \cdot \dot{\mathbf{h}} = \boldsymbol{\sigma} : \dot{\boldsymbol{\varepsilon}} - \rho \dot{\psi} - \rho s \dot{\theta} - \mathbf{X}_p : \dot{\boldsymbol{\varepsilon}}_p - \mathbf{X}_g : \dot{\mathbf{g}}; \quad (11)$$

$$X = \int_{\boldsymbol{\varepsilon}_1}^{\boldsymbol{\varepsilon}_2} \boldsymbol{\sigma} : d\boldsymbol{\varepsilon} - \rho (\psi_2 - \psi_1) - \int_{\theta_1}^{\theta_2} \rho s d\theta - \int_0^{t_p} (\mathbf{X}_p : \dot{\boldsymbol{\varepsilon}}_p + \mathbf{X}_g : \dot{\mathbf{g}}) dt. \quad (12)$$

Taking into account the decomposition (1) and eqn (7)₁ for \mathbf{X}_p we obtain

$$X = \int_{\boldsymbol{\varepsilon}_1}^{\boldsymbol{\varepsilon}_2} \boldsymbol{\sigma} : d(\boldsymbol{\varepsilon}_e + \boldsymbol{\varepsilon}_\theta) - \rho (\psi_2 - \psi_1) - \int_{\theta_1}^{\theta_2} \rho s d\theta + \int_{\mathbf{g}_1}^{\mathbf{g}_2} \rho \frac{\partial \psi}{\partial \mathbf{g}^i} : d\mathbf{g} + \int_{\boldsymbol{\varepsilon}_{p1}}^{\boldsymbol{\varepsilon}_{p2}} \rho \frac{\partial \psi}{\partial \boldsymbol{\varepsilon}_p} : d\boldsymbol{\varepsilon}_p. \quad (13)$$

At $(\partial \psi) / (\partial \boldsymbol{\varepsilon}_p) = 0$ Eq.(13) is more suitable for application, because in this case the plastic strain $\boldsymbol{\varepsilon}_p$ disappears completely. Eq.(12) shows that X is the total dissipation increment minus plastic dissipation increment and the dissipation increment due to the internal variables.

Nucleation and interface propagation conditions. Kinetic equation. PT cannot occur at a single material point, because the surface energy per unit transforming volume will be infinite. In reality PT takes place in some finite volume. That is why it is necessary to consider the total dissipation rate $\bar{\mathcal{D}}_\xi$ due to PT in the transforming volume V_n and to take into account the surface energy:

$$\bar{\mathcal{D}}_\xi := X_v \dot{\chi}; \quad X_v := \int_{V_n} X dV_n - \int_{\Sigma_n} \gamma d\Sigma_n, \quad (14)$$

where Σ_n is the surface of the nucleus and γ is the change in surface energy per unit area after the PT, X_v and $\dot{\chi}$ are the dissipative force and rate respectively. Alternatively,

$$\bar{\mathcal{D}}_\xi := \frac{1}{V_n} X_v \frac{V_n}{t_p} = \bar{X} \dot{V}_n, \quad \text{where} \quad \bar{X} := \frac{1}{V_n} X_v \quad \text{and} \quad \dot{V}_n := \frac{V_n}{t_p} \quad (15)$$

is the dissipative force and rate. We will use the second definition. For the reverse PT $\dot{V}_n := -\frac{V_n}{t_p}$ [4].

As is usual in irreversible thermodynamics, the kinetic equation between force and rate $\dot{V}_n = f(\bar{X}, \dots)$ or $\bar{X} = k(\dot{V}_n, \dots)$ has to be given. Functions f and k can depend on θ , $\boldsymbol{\varepsilon}_p$, \mathbf{g} , V_n , ... and should be determined experimentally. Sometimes it is convenient to present $k = \frac{1}{V_n} \int_{V_n} \tilde{k} dV_n$, where \tilde{k} is a locally determined function. There are only two possibility for the behaviour of the function k as $\dot{V}_n \rightarrow 0$.

1. Let the condition $\dot{V}_n = 0$ be valid at $\bar{X} = 0$ only, then the macroscopically equilibrium PT ($\dot{V}_n \rightarrow 0$) can be described with the equation $\bar{X} = 0$.

2. Let

$$\text{at} \quad \dot{V}_n = 0 \quad k_{2 \rightarrow 1}^0 \leq \bar{X} \leq k_{1 \rightarrow 2}^0,$$

$$\text{at} \quad \dot{V}_n > 0 \quad \bar{X} = k_{1 \rightarrow 2}(\dot{V}_n, \dots) > 0, \quad \text{at} \quad \dot{V}_n < 0 \quad \bar{X} = k_{2 \rightarrow 1}(\dot{V}_n, \dots) < 0, \quad (16)$$

where $k_{1 \rightarrow 2}^0$ and $k_{2 \rightarrow 1}^0$ are the threshold values of \bar{X} at the direct and the reverse PT. In this case there is *thermodynamic hysteresis*, i.e. direct and reverse PT begin at different values \bar{X} and between these values PT is impossible. In the first case there is no hysteresis. For most martensitic transformations the values $k_{1 \rightarrow 2}^0$ and $|k_{2 \rightarrow 1}^0|$ are very high. We assume here finite k^0 as well. The case $k^0 = 0$ will be considered as a particular case of Eq.(16). Substituting Eq.(12) for X

in Eq.(16), we obtain for nucleation condition during time t_p in volume V_n

$$\begin{aligned} \int_{V_n} \int_{\boldsymbol{\varepsilon}_1}^{\boldsymbol{\varepsilon}_2} \boldsymbol{\sigma} : d\boldsymbol{\varepsilon} dV_n &= \int_t^{t+\Delta t} \int_{\Sigma_n} \mathbf{p} \cdot \mathbf{v} d\Sigma_n dt = \int_{\Sigma_n} \gamma d\Sigma_n + \int_{V_n} \rho (\psi_2 - \psi_1) dV_n + \\ + \int_{V_n} \int_{\theta_1}^{\theta_2} \rho s d\theta dV_n &+ \int_{V_n} \int_t^{t+\Delta t} (\mathbf{X}_p : \dot{\boldsymbol{\varepsilon}}_p + \mathbf{X}_g : \dot{\mathbf{g}}) dt dV_n + \int_{V_n} \bar{k} (\dot{V}_n) dV_n, \end{aligned} \quad (17)$$

where \mathbf{v} is the velocity on Σ_n from the side of nucleus. Note that Gauss theorem was used.

In order to derive an interface propagation condition we assume that the volume V_n is obtained by *interface* Σ propagation with a normal velocity v_n in time $\Delta t = t_p$, i.e. it is bounded by surfaces Σ_t and $\Sigma_{t+\Delta t}$ at time t and $t + \Delta t$ respectively, as well as by two lateral infinitesimal surfaces with the heights $v_n \Delta t$, $dV_n = v_n \Delta t d\Sigma$. Using Hadamard compatibility condition and traction continuity it is possible to simplify the stress work integral in Eq.(17) and to avoid the integration over the deformation process. Neglecting for simplicity of surface energy and assuming that each point of an interface can move independently of another points we can derive [4]

$$\mathbf{n} \cdot \boldsymbol{\sigma} \cdot [\mathbf{F}] \cdot \mathbf{n} = \boldsymbol{\sigma} : [\boldsymbol{\varepsilon}] = \rho [\psi] + \int_{\theta_1}^{\theta_2} \rho s d\theta + \int_t^{t+\Delta t} (\mathbf{X}_p : \dot{\boldsymbol{\varepsilon}}_p + \mathbf{X}_g : \dot{\mathbf{g}}) dt + \bar{k}. \quad (18)$$

Here \mathbf{n} is the unit normal to the interface, $\mathbf{F} = \mathbf{I} + \boldsymbol{\varepsilon} + \boldsymbol{\omega}$, $\boldsymbol{\omega}$ the rotation tensor, \mathbf{I} the unit tensor; $[\mathbf{a}] := \mathbf{a}_2 - \mathbf{a}_1$. Eq.(18) have to be valid at time $t + \Delta t$ as well [4], which results in additional equation, similar to consistency condition in plasticity theory.

Extremum principle for determination of unknown parameters. The kinetic Eq. (16) is only one scalar equation which is not sufficient for the determination of all unknown parameters. To determine all unknown parameters \mathbf{b} , e.g. position, shape, volume and orientation of nucleus, jump of $\boldsymbol{\varepsilon}$ and plastic deformation $\boldsymbol{\varepsilon}_p$, related to $\boldsymbol{\varepsilon}_p$ temperature evolution, as well as functions $\boldsymbol{\varepsilon}(\xi)$, $\boldsymbol{\varepsilon}_p(\xi)$, $\theta(\xi)$ and so on, let us use the postulate of realizability [4, 7]. Let for the given boundary conditions and arbitrary fixed \dot{V}_n

$$\bar{X}(\mathbf{b}^*) - k(\dot{V}_n, \mathbf{b}^*) < 0 \quad (19)$$

for all possible PT parameters \mathbf{b}^* , i.e. PT cannot occur with this \dot{V}_n . If in the course of continuous variation of boundary conditions and for each boundary conditions continuous variation of all admissible parameters \mathbf{b}^* the condition (16) is fulfilled the *first* time for some of parameters \mathbf{b} , then PT will occur with these \mathbf{b} and \dot{V}_n (if condition (16) is not violated in the course of PT, e.g. interface propagation).

If, in the course of continuous variation of boundary conditions and for each boundary conditions continuous variation of all admissible parameters \mathbf{b}^* the equality (16) is met the first time for one or several \mathbf{b} , then for arbitrary other \mathbf{b}^* inequality (19) should be held, as in the opposite case for this \mathbf{b}^* condition (16) had to be met before it was satisfied for \mathbf{b} . Consequently, we obtain the extremum principle for determination of all unknown parameters \mathbf{b} :

$$\bar{X}(\mathbf{b}) - k(\dot{V}_n, \mathbf{b}) = 0 > \bar{X}(\mathbf{b}^*) - k(\dot{V}_n, \mathbf{b}^*). \quad (20)$$

3. Some specifications. Determination of temperature.

Let

$$\rho \psi_i = 0.5 \boldsymbol{\varepsilon}_{ei} : \mathbf{E}_i : \boldsymbol{\varepsilon}_{ei} + \rho \psi_i^e = \rho \psi_i^e + \rho \psi_i^{\theta}, \quad i = 1, 2, \quad (21)$$

where ψ_i^ε and ψ_i^θ are the elastic and thermal parts of free energy. Since

$$\int_{\boldsymbol{\varepsilon}_{e_1}}^{\boldsymbol{\varepsilon}_{e_2}} \boldsymbol{\sigma} : d\boldsymbol{\varepsilon}_e = \rho (\psi_2^\varepsilon - \psi_1^\varepsilon) - 0.5 \int_{\mathbf{E}_1}^{\mathbf{E}_2} \boldsymbol{\varepsilon}_e : d\mathbf{E}(\boldsymbol{\xi}) : \boldsymbol{\varepsilon}_e \quad (22)$$

(see [4]), it follows then from Eq.(13)

$$\begin{aligned} X &= \int_{\boldsymbol{\varepsilon}_1}^{\boldsymbol{\varepsilon}_2} \boldsymbol{\sigma} : d\boldsymbol{\varepsilon}_\theta - 0.5 \int_{\mathbf{E}_1}^{\mathbf{E}_2} \boldsymbol{\varepsilon}_e : d\mathbf{E}(\boldsymbol{\xi}) : \boldsymbol{\varepsilon}_e - \rho (\psi_2^\theta - \psi_1^\theta) - \int_{\theta_1}^{\theta_2} \rho s d\theta + \\ &+ \int_{\mathbf{g}_1}^{\mathbf{g}_2} \rho \frac{\partial \psi}{\partial \mathbf{g}^t} : d\mathbf{g} + \int_{\boldsymbol{\varepsilon}_{p_1}}^{\boldsymbol{\varepsilon}_{p_2}} \rho \frac{\partial \psi}{\partial \boldsymbol{\varepsilon}_p} : d\boldsymbol{\varepsilon}_p. \end{aligned} \quad (23)$$

Generally $\boldsymbol{\varepsilon}_\theta = \boldsymbol{\alpha}(\theta - \theta_o)$, where $\boldsymbol{\alpha} = \boldsymbol{\alpha}(\boldsymbol{\xi}, \theta - \theta_o)$ and θ_o is the reference temperature. For the determination of a temperature variation in the course of PT we can use an entropy balance equation

$$\rho \theta \dot{s} = \mathcal{D} + \operatorname{div} \mathbf{h} + \frac{\nabla \theta}{\theta} \cdot \mathbf{h}. \quad (24)$$

Substitution of an expression (6) for the rate of dissipation \mathcal{D} in Eq.(24) yields

$$\rho \theta \dot{s} = \operatorname{div} \mathbf{h} + \mathbf{X}_p : \dot{\boldsymbol{\varepsilon}}_p + \mathbf{X}_g : \dot{\mathbf{g}} + X_\xi \dot{\boldsymbol{\xi}}. \quad (25)$$

According to Eq.(5)₂ $s = s(\theta, \boldsymbol{\sigma}, \mathbf{g}, \boldsymbol{\varepsilon}_p, \boldsymbol{\xi})$. Substitution of this expression and Eq.(9)₃ for the heat flux into Eq.(25) leads to the temperature evolution equation

$$\begin{aligned} \rho \nu \dot{\theta} &= \operatorname{div} \mathbf{f}_h \left(-\frac{\nabla \theta}{\theta} \right) + \left(\mathbf{X}_p - \rho \frac{\partial s}{\partial \boldsymbol{\varepsilon}_p} \theta \right) : \dot{\boldsymbol{\varepsilon}}_p + \left(\mathbf{X}_g - \rho \frac{\partial s}{\partial \mathbf{g}} \theta \right) : \dot{\mathbf{g}} + \\ &+ \left(X_\xi - \rho \frac{\partial s}{\partial \boldsymbol{\xi}} \theta \right) \dot{\boldsymbol{\xi}} - \rho \theta \frac{\partial s}{\partial \boldsymbol{\sigma}} : \dot{\boldsymbol{\sigma}}, \quad \nu := \theta \frac{\partial s}{\partial \theta}, \end{aligned} \quad (26)$$

where ν is the specific heat at constant $\boldsymbol{\sigma}$, \mathbf{g} , $\boldsymbol{\varepsilon}_p$ and $\boldsymbol{\xi}$. For the *adiabatic* process $\operatorname{div} \mathbf{h} = 0$ and Eq.(26) determines the temperature evolution in each material point independently.

Let us consider some specifications of Eq.(26). Assume the validity of Eq.(21) for the free energy and constant elastic moduli, specific heats and thermal expansion tensors in each phase. Then from the conditions $\nu := \theta \frac{\partial s}{\partial \theta}$ and $\boldsymbol{\sigma} = \frac{\partial \psi}{\partial \boldsymbol{\varepsilon}_e} = \mathbf{E} : \boldsymbol{\varepsilon}_e$ and Eq.(5)₂ we derive explicit expressions for the entropy and the thermal part of the free energy for each phase and for the material in the process of SOPT:

$$\rho s_i = \rho s_{oi} + \rho \nu_i \ln \theta / \theta_o + \boldsymbol{\sigma} : \boldsymbol{\alpha}_i, \quad i = 1, 2; \quad (27)$$

$$\psi_i^\theta = \psi_{oi} - s_{oi} (\theta - \theta_o) - \nu_i \theta (\ln \theta / \theta_o - 1) - \nu_i \theta_o; \quad (28)$$

$$\rho s = \rho s_o(\boldsymbol{\xi}) + \rho \nu(\boldsymbol{\xi}) \ln \theta / \theta_o + \boldsymbol{\sigma} : \boldsymbol{\alpha}(\boldsymbol{\xi}); \quad (29)$$

$$\psi^\theta = \psi_o(\boldsymbol{\xi}) - s_o(\boldsymbol{\xi}) (\theta - \theta_o) - \nu(\boldsymbol{\xi}) \theta (\ln \theta / \theta_o - 1) - \nu(\boldsymbol{\xi}) \theta_o. \quad (30)$$

Here s_{oi} and ψ_{oi} are the constants. If $\theta_o = \theta_e$, then by the definition of equilibrium temperature θ_e we have $\psi_{o1} = \psi_{o2} = \psi_o$ and the transformation entropy $s_t = s_{o2} - s_{o1}$. For generalized SOPT by definition $s_t = 0$ and $s_{o2} = s_{o1} = s_o$.

Functions $\mathbf{E}(\boldsymbol{\xi})$, $\nu(\boldsymbol{\xi})$ and $\boldsymbol{\alpha}(\boldsymbol{\xi})$ are usually unknown and we assume a linear approximation

$$\mathbf{E} = (1 - \boldsymbol{\xi}) \mathbf{E}_1 + \boldsymbol{\xi} \mathbf{E}_2, \quad \nu = (1 - \boldsymbol{\xi}) \nu_1 + \boldsymbol{\xi} \nu_2, \quad \boldsymbol{\alpha} = (1 - \boldsymbol{\xi}) \boldsymbol{\alpha}_1 + \boldsymbol{\xi} \boldsymbol{\alpha}_2. \quad (31)$$

Then Eq.(26) can be transformed into the form

$$\rho \nu(\xi) \dot{\theta} = (X_\xi - \rho \Delta \nu \theta \ln \theta / \theta_o - \sigma : \Delta \alpha \theta) \dot{\xi} - \dot{\sigma} : \alpha(\xi) \theta + \mathbf{X}_p : \dot{\epsilon}_p + \mathbf{X}_g : \dot{g}, \quad (32)$$

where $\Delta \mathbf{b} := \mathbf{b}_2 - \mathbf{b}_1$ and independence of s_o of \mathbf{g} and ϵ_p is assumed. According to Eq.(8)

$$X_\xi = \sigma : \Delta \alpha(\theta - \theta_o) - 0.5 \epsilon_e : \Delta \mathbf{E} : \epsilon_e - \rho \Delta \nu(\theta - \theta_o) + \rho \Delta \nu \theta \ln \theta / \theta_o \quad (33)$$

and Eq.(32) can be transformed into

$$\rho \nu(\xi) \dot{\theta} = (-\sigma : \Delta \alpha \theta_o - 0.5 \epsilon_e : \Delta \mathbf{E} : \epsilon_e - \rho \Delta \nu(\theta - \theta_o)) \dot{\xi} - \dot{\sigma} : \alpha(\xi) \theta + \mathbf{X}_p : \dot{\epsilon}_p + \mathbf{X}_g : \dot{g}. \quad (34)$$

In contrast to [4] we did not use the simplifying assumption $X_\xi = k$. If ψ_o is independent of \mathbf{g} and ϵ_p , then $\mathbf{X}_g = 0$ and $\mathbf{X}_p = \sigma$.

4. Fracture in inelastic materials

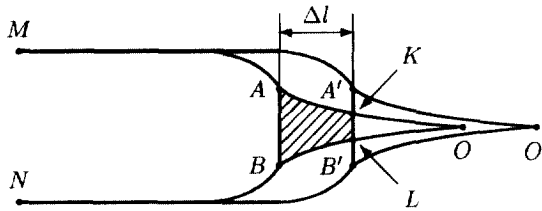


Fig. 1. Crack position MAOBN before and MA'O'B'N after crack advance by distance Δl; ABLK is the fracture zone.

Definition. We will apply now a theory developed for the description of fracture, namely pore and crack nucleation and growth. We will define fracture as a thermomechanical process of change in some region of elastic moduli, heat capacity, thermal expansion coefficient and yield strength from initial values to zero, which is accompanied by change in entropy, hardening rules and so on.

This process cannot be stopped at a material point in the intermediate state.

We will not limit the change in transformation entropy, because we do not know whether it corresponds to reality. Conventionally we can consider the material at each point as a mixture of vacuum with zero properties and volume fraction ξ and unfractured material. Then the fracture is a process of growth of ξ from 0 to 1. The actual fracture region and in particularly its dimension can be found from extremum principle (20). For elastic materials, at quasi-static isothermal process without dissipation due to fracture (k = 0), with neglected thermal expansion and heat capacity the fracture criterion and extremum principle (20) are equivalent to those obtained using the principle of the minimum of Gibbs energy [4]. Consequently in this case our approach has to give the same results as classical energetic methods in fracture mechanics [8, 9]. As an example of a kinetic equation we consider

$$\bar{X} = k^0 + E_a + \frac{n}{V_n N} R \theta \ln \frac{\dot{V}_n}{\dot{V}_0}, \quad (35)$$

which leads to threshold-type and size-dependent generalization of Arrhenius-type kinetics

$$\dot{V}_n = \dot{V}_0 \exp \left(\frac{(\bar{X} - k^0 - E_a) V_n N}{R \theta} \right) \quad \text{at} \quad 0 \leq \bar{X} - k^0 \leq E_a, \quad (36)$$

$$\dot{V}_n = 0 \quad \text{at} \quad \bar{X} - k^0 < 0. \quad (37)$$

Here E_a is the activation energy per unit volume at $\bar{X} - k^0 = 0$, $R = 8.314 \text{ J/(K mol)}$ is the gas constant, \dot{V}_0 is some characteristic rate, n the number of atoms in volume V_n which

undergo thermal fluctuations, $N = 6.02 \cdot 10^{23}$ is Avogadro's number (number of atoms in 1 mol). In Eq.(36) 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.(37) is related to the fulfillment of 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.(36) loses its sense.

For inelastic materials all energetic crack propagation criteria have the following form: some driving force has to reach its critical value. As a driving force an energy flow in an infinitesimal or finite-sized process zone [8-11], plastic work [12], total dissipation rate [13, 14] and so on are assumed. In most papers it is recognized that these driving forces include not only the energy necessary for a fracture process, but for plastic straining as well and it was not clear how to separate these processes. Consequently the strict thermodynamic fracture criterion was lacking.

The approach suggested in the given paper strictly separates the dissipation rate due to fracture only and expresses it as a product of dissipative force \bar{X} and rate \dot{V}_n . Then the standard procedure in irreversible thermodynamics of connecting rate and force leads to time-independent or time-dependent fracture kinetics.

It is important that the approach developed is valid for an arbitrary dissipative material, because the material's constitutive equations are not used in the derivation. For an arbitrary material and a quasi-static or dynamic process the dissipation increment due to fracture only is a difference between the total dissipation increment and the dissipation increment due to all other processes excluding fracture. That is why parameter $\int X dV_n$ can be calculated by integration over an arbitrary region which includes region V_n with fracture (because outside V_n we have $X = 0$), i.e. it is a region-independent integral.

A general scheme for the application of PT or fracture criterion and extremum principle (20), as well as the temperature evolution equation (26) (with an additional heat source $-s_t \theta_0 \xi$) is as follows. All material properties and constitutive equations (9) must be given as a function of ξ . Then assume that at some initial conditions and prescribed increment of boundary conditions fracture occurs in some region V_n . We reduce incrementally in some way the elastic moduli, heat capacity, thermal expansion coefficient and yield strength from initial values to 0 in a possible fracture region. After solving the elastoplastic and thermal boundary-value problems for each step we determine the variation of all fields, calculate the driving force \bar{X} and resistance k and determine the fracture rate \dot{V}_n and consequently the fracture time t_p from equality $\bar{X} = k(\dot{V}_n)$. Then we vary the possible fracture region and way of reducing of elastic moduli, heat capacity, thermal expansion coefficient and yield strength from initial values to 0 in it (homogeneously or heterogeneously) and find such a fracture region and way of reducing of properties which maximize the difference $\bar{X} - k$. The final fracture rate and time in this region are determined again by equality $\bar{X} = k(\dot{V}_n)$.

Pore nucleation. Let us consider a spherically symmetrical problem on pore nucleation in an elastic-perfectly-plastic space under a homogeneously distributed tensile stress p . We will model this process by decreasing in a compression modulus in a small sphere with a radius r from an initial value to zero under isothermal conditions. The stress state for this problem can be found for example in [15]. After a simple calculation we obtain

$$X = -0.5 \int_{\mathbf{B}} \boldsymbol{\varepsilon}_e : d\mathbf{E} : \boldsymbol{\varepsilon}_e = \frac{3}{4} \frac{(1 - \nu_0)}{E} \left(\frac{2}{3} \sigma_y \right)^2 \left[2 \exp \left(\frac{p}{2/3 \sigma_y} - 1 \right) - 1 \right], \quad (38)$$

where E , ν_0 and σ_y are Young's modulus, the Poisson ratio and the yield stress of the parent material. The transformation condition (35) reads as

$$\left(X - k^0 - E_a \right) \frac{4}{3} \pi r^3 - \gamma 4 \pi r^2 - \frac{n}{N} R \theta \ln \frac{\dot{V}_n}{\dot{V}_0} = 0. \quad (39)$$

Maximizing the left part of Eq.(39) with respect to r (according to principle (20)) we obtain $r \rightarrow \min$. The minimum value of r can be found from condition $\bar{X} = k^0$, i.e.

$$\left(X - k^0 \right) \frac{4}{3} \pi r_t^3 - \gamma 4 \pi r_t^2 = 0 \quad \text{or} \quad r_t = \frac{3 \gamma}{X - k^0}. \quad (40)$$

Substitution of (40) in Eq.(36) results in

$$\dot{V}_n = \dot{V}_0 \exp \left(- \frac{E_a}{R \theta} \frac{N}{n} \frac{4}{3} \pi r_t^3 \right); \quad t_p = \frac{4 \pi r_t^3}{3 \dot{V}_n}. \quad (41)$$

Let us analyze the results. If at given p the value X exceeds k^0 , then a pore with radius r_t appears during the shortest possible time determined by Eq.(41). We will call a nucleus (pore) with a radius r_t the *thermodynamically admissible nucleus*. It has nothing in common with the usual critical nucleus, which is determined by minimization (not maximization) of the left side of Eq.(40)₁ with respect to r (usually at $k^0 = 0$). It is evident that for a critical nucleus $\bar{X} - k^0 < 0$, i.e. its appearance is impossible from the point of view of the nucleation criterion and at $k^0 = 0$ *contradicts the second law of thermodynamics*. In contrast to the usual approach, we determine a thermodynamically admissible nucleus in terms of kinetics: this is nucleus with possible minimum size which can appear from point of view of thermodynamics and appears with the possible highest rate. According to Eq.(39), X or \bar{X} satisfy "static" fracture condition (as for rate-independent kinetics). Increase in X reduces radius of thermodynamically admissible nucleus, which leads to growth of the rate of transformation in Eq.(41).

Crack propagation. As the next example we derive equation for crack propagation in elastic perfectly plastic material in the framework similar to Dugdale model [8, 9] for plane stress case. Localized plastic region OAB (Fig. 1) in front of crack is under action of cohesive (restraining) stresses $\sigma = \sigma_y$ on the extended crack surfaces OA and OB, the separation distance δ between these surfaces is determined by known formulae [8, 9]. We will use the following interpretation: at crack propagation by a distance Δl fracture occurs in the finite region *ABLK*. We will take into account stress and elastic strain normal to crack plane only, other components are neglected. Additionally we assume that during the fracture process

$$E(\xi) = E(1 - \xi); \quad \sigma_y(\xi) = \sigma_y(1 - \xi), \quad \text{i.e.} \quad \varepsilon_e = \frac{\sigma_y(\xi)}{E(\xi)} = \frac{\sigma_y}{E} = \text{const.} \quad (42)$$

Then calculation of X according to Eq.(38) results in $X = 0.5 \sigma_y^2 / E$. The transforming volume before transformation is $V_1 = b \Delta l \bar{\delta}$, where $\bar{\delta}$ is some intermediate value of crack opening at the length Δl and b is the thickness of thin sheet. The kinetic Eq.(35) reads as

$$\left(0.5 \frac{\sigma_y^2}{E} - k^0 - E_a \right) b \Delta l \bar{\delta} - 2 \gamma \Delta l b - \frac{n}{N} R \theta \ln \frac{\dot{V}_n}{\dot{V}_0} = 0. \quad (43)$$

Maximizing the left part of Eq.(43) with respect to Δl and $\bar{\delta}$ (according to principle (20)) we obtain $\Delta l \bar{\delta} \rightarrow \min$. The minimum value of $\bar{\delta}$ can be found from condition $\bar{X} = k^0$, i.e.

$$\left(0.5 \frac{\sigma_y^2}{E} - k^0 \right) b \Delta l \bar{\delta} - 2 \gamma \Delta l b = 0. \quad (44)$$

Condition $\Delta l \rightarrow \min$ results in $\Delta l = a$, where a is the interatomic distance in direction of crack propagation. Then $\bar{\delta} = \delta$, where δ is the crack opening displacement between points A and B and thermodynamic fracture criterion (44) reduces to criterion of critical crack opening

$$\delta = \delta_c := \frac{2 \gamma}{0.5 \sigma_y^2 / E - k^0}. \quad (45)$$

It follows from the Dugdale model that $\delta = \frac{J}{\sigma_y}$, where J is the path independent J -integral calculated over the path not passing through plastic region. Then criterion (45) can be represented as criterion of critical value of J -integral

$$J = J_c := \sigma_y \delta_c = \sigma_y \frac{2\gamma}{0.5 \sigma_y^2 / E - k^0}. \quad (46)$$

Kinetic equation of crack growth (36) results in

$$\dot{V}_n = \frac{ba\delta_c}{t_p} = \dot{V}_0 \exp\left(-\frac{E_a}{R\theta} \frac{N}{n} ba\delta_c\right). \quad (47)$$

5. Concluding remarks

A suggested theory of SOPT and fracture in inelastic materials is a particular case and a specification of the theory of FOPT developed in [4]. That is why it is easy to take large deformations and displacement discontinuity into account in the same way as in [4]. Path-independent integrals [8, 9, 11, 16], which are an ideal tool for the description of various phenomena in elastic media, are not sufficient for inelastic materials. Instead, region-independent integrals, developed for the description of FOPT in [4] and applied here for SOPT and fracture in inelastic materials, can hopefully be applied to other processes in inelastic materials, like point defects, dislocations and disclinations nucleation, solid state chemical reactions, deformation of amorphous materials, diffusional-displacive PT and so on. Methods of control of FOPT [17] will probably be useful for the generalized SOPT.

Acknowledgment – The support of Volkswagen Foundation, as well as discussions with Prof. Erwin Stein are gratefully acknowledged.

References

- [1] Landau L. D., Lifshitz E. M., *Statistical Physics*. Part 1 (1976) Moscow, Nauka.
- [2] Grinfeld M. A., *Mekhanika Tverdogo Tela* **5** (1979) 95-102.
- [3] Grinfeld M. A., *Thermodynamic Methods in the Theory of Heterogeneous Systems* (1991) Longman, Sussex.
- [4] Levitas V. I., *Int. J. Solids and Structures* **35** (1998) 889-940.
- [5] Fischer F.D., Berveiller M., Tanaka K., Oberaigner E., *Arch. Appl. Mech.* **64** (1994) 54-85.
- [6] Landau L. D., Lifshitz E. M., *Electrodynamics of continuous media*. Moscow, Nauka (1976).
- [7] Levitas V. I., *Int. J. Eng. Sci.*, Part 1 and 2, **33** (1995) 921-971.
- [8] Rice J. R., in: *Fracture. An Advanced Treatise* (ed. H. Liebowitz) **2**, Academic Press, N.Y. – London (1968) 191-311.
- [9] Cherepanov G. P., *Mechanics of Brittle Fracture*. McGraw Hill N.Y. 1979
- [10] Hutchinson J. W., *Trans. ASME, ser. E., J. Appl. Mech.* **50** (1983) 1042-1051.
- [11] Atluri S. N., *Structural Integrity & Durability* (1997) Tech Science Press, Forsyth.
- [12] Kuang J. H., Chen Y. C., *Engineering Fracture Mechanics* **58** (1997) 61-70.
- [13] Turner C. E., Kolednik O., *Fatigue Fract. Engng Mater. Struct.* **20** (1997) 1507-1528.
- [14] Kolednik O., Shan G., Fischer D. F., in: *Fatigue and Fracture Mechanics* **27**, ASTM STP 1296, (eds. R. S. Piascik, J. C. Newman and N. E. Dowling) (1997) 126-151.
- [15] Roitburd A. L. and Temkin D. E., *Sov. Phys. Solid State*, **28** (1986) 432-436.
- [16] Eshelby J. D., *Solid State Physics* **3** (1956) 79-144, New York: Academic Press.
- [17] Levitas V. I., *J. Mech. Phys. Solids* **45** (1997) 923-947 and 1203-1222.