NEW MODEL OF THE PHASE TRANSITION KINETICS IN SOLIDS

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Summary The kinetics of phase transition in thermoelastic materials is considered. The model is based on the local balance of energy and takes into account the latent energy of transition. Some general restrictions such as non-negativity of dissipation; thermomechanical thresholds, interrelation of the phase transition character (reversibility and irreversibility) with kinetic parameter are discussed. The model is illustrated on one-dimensional example.

BASIC RELATIONS ON INTERFACE

The quasistatic thermal and mechanical loading of thermoelastic material is considered. Deformations are supposed to be small. The material is undergoing to phase transition of the first kind. The relations [1is3]

$$[\mathbf{u}]=0,\quad [\theta]=0,\quad [\rho c]=0,\quad [\nabla\otimes\mathbf{u}]=\mathbf{n}\otimes\mathbf{h},\quad [\boldsymbol{\sigma}]\cdot\mathbf{n}=0,\quad [\rho\psi]=\mathbf{n}\cdot\boldsymbol{\sigma}\cdot\mathbf{h}+\delta_* \tag{1}$$

are valid on interface moving with velocity c in a direction $\mathbf{n}$. Here ψ is a density of free energy, $\boldsymbol{\sigma}$ is a stress tensor, $\mathbf{e}$ is a tensor of small deformations, δ_* is a source of entropy concentrated on interface, $\mathbf{v}$ is a mass velocity, vector $\mathbf{h}=-[\mathbf{v}]/c$. The relations (1) are obtained assuming that the singular sources of mass, momentum and energy are absent on interface. Strain compatibility follows from displacement continuity. As to singular sources of entropy, the case $\delta_*=0$ corresponds to *reversible* phase transformation, $\delta_*>0$ corresponds to *irreversible* phase transition. The important consequence of (1) is a condition for jump of components of the chemical potential tensor [4]

$$\mathbf{n}\cdot[\boldsymbol{\chi}]\cdot\mathbf{n}=\delta_*,\qquad \boldsymbol{\chi}\equiv\psi\mathbf{I}-\rho^{-1}\left(\boldsymbol{\sigma}\cdot\mathbf{e}+\mathbf{e}\cdot\boldsymbol{\sigma}-(\mathbf{e}:\mathbf{I})\boldsymbol{\sigma}\right). \tag{2}$$

EQUATIONS OF TWO - PHASE MIXTURE

We consider a thermodynamic potential of two - phase mixture. Both phases are assumed isotropic thermoelastic solids. The deviation of temperature from initial value is small. The scalar structural parameter ω is equal to mass concentration of the second phase. An initial state of material is natural. The free energy is written in the new form

$$\begin{gathered}\psi(\mathbf{e},\vartheta,\omega)=\psi_{pt}(\omega)+(1-\omega)\psi^{(1)}(\mathbf{e},\vartheta)+\omega\psi^{(2)}(\mathbf{e},\vartheta),\qquad \rho\psi_{pt}(\omega)=g\omega+\frac{1}{n+1}b\omega^{n+1},\qquad g,b>0,\ n\ge 1\\ \rho\psi^{(1)}(\mathbf{e},\vartheta)=\tfrac{1}{2}K_1I_1^2(\mathbf{e})+\mu_1J^2(\mathbf{e})-\alpha_1\vartheta I_1(\mathbf{e})-\tfrac{1}{2}c_1\vartheta^2\\ \rho\psi^{(2)}(\mathbf{e},\vartheta)=-p_0I_1(\mathbf{e})-\rho\eta_0\vartheta+\tfrac{1}{2}K_2I_1^2(\mathbf{e})+\mu_2J^2(\mathbf{e})-\alpha_2\vartheta I_1(\mathbf{e})\end{gathered} \tag{3}$$

Here $\psi_{pt}(\omega)$ is a *latent energy* of transformation of the first phase into second one, $\psi^{(i)}$ is free energy of phases equal to zero at $\mathbf{e}=0,\vartheta=0$. The value $\psi_{pt}(0)=0,\ \psi_{pt}(1)=\psi_0$, where ψ_0 is the latent energy of complete transformation. Values $I_1=\mathbf{e}:\mathbf{I},\ J^2=dev\mathbf{e}:dev\mathbf{e}$ are the invariants of strain tensor, α_i are factors of thermal expansion, K_i,μ_i are elastic modules, c_i are heat capacities, p_0,η_0 are pressure and entropy of the second phase in state $\mathbf{e}=0,\vartheta=0,\omega=1$.

To formulate the kinetic equation we use the local inequality of entropy [5] $\rho\theta\dot\eta-\theta\nabla\cdot(\theta^{-1}\mathbf{q})-\rho r\ge 0$, where η is specific entropy, $\mathbf{q}$ is a heat flux, r is a density of heat sources. This inequality together with formulas (3) gives

$$\begin{gathered}\boldsymbol{\sigma}(\mathbf{e},\vartheta,\omega)=\rho\partial\psi/\partial\mathbf{e}=(\hat K(\omega)I_1-\hat\alpha(\omega)\vartheta-\omega p_0)\mathbf{I}+2\hat\mu(\omega)\mathbf{e}',\\ \rho\eta(\mathbf{e},\vartheta,\omega)=-\rho\partial\psi/\partial\theta=\hat\alpha(\omega)I_1+\hat c(\omega)\vartheta+\omega\rho\eta_0,\qquad \hat a(\omega)=(1-\omega)a_1+\omega a_2,\quad a=K,\mu,\alpha,c\\ \delta_{pt}\equiv-\rho\dot\omega\,\partial\psi(\mathbf{e},\vartheta,\omega)/\partial\omega\ge 0,\qquad \delta_{pt}+\theta^{-1}\mathbf{q}\left(\mathbf{e},\vartheta,\omega,\nabla\vartheta\right)\cdot\nabla\vartheta\ge 0,\end{gathered} \tag{4}$$

where δ_{pt} is the *dissipation of structural transformation*. The kinetic equation $\dot\omega=-A\partial\psi(\mathbf{e},\vartheta,\omega)/\partial\omega$, where $A=(\tau b)^{-1}H(\omega)H(1-\omega)\ge 0$, or

$$\dot\omega+\beta\omega^n=\beta\Phi(\mathbf{e},\vartheta),\quad \Phi\equiv\tfrac{1}{2}\Delta KI_1^2+\Delta\mu J^2-\Delta\alpha\vartheta I_1-\tfrac{1}{2}\Delta c\vartheta^2+b^{-1}(p_0I_1+\rho\eta_0\vartheta-g),\quad \beta\equiv\tau^{-1}H(\omega)H(1-\omega) \tag{5}$$

is a *sufficient condition* for $\delta_{pt}\ge 0$ in any processes. Here $\Delta a\equiv(a_1-a_2)/b,\ a_i=K_i,\mu_i,\alpha_i,c_i$. The quantity τ is a relaxation time due to structural change, $H(x)$ is a stepwise function. The derivative $-\partial\psi/\partial\omega$ is a «driving force» of phase transition. In direct transition this force characterizes the balance between the energy released due to partial unloading of a material in vicinity of new phase nucleus and the absorbed energy spent to growth of latent energy. In backward transition the situation is directly opposite.

The interdependence between the transition rate and the difference of chemical potentials of phases are widely used for the phase transitions kinetics [6-9]. The peculiarity of the model developed consists in explicit usage of latent energy, which depends on the depth of transformation. It should be noted that if the difference of entropy in initial state is large $\rho\eta_0/b=O(1)$ then the term $\rho b^{-1}\eta_0\vartheta$ in (5) is greater then other terms, and the kinetics is linear on temperature. The structural transitions are determined only by thermal effects [6]. In this case the influence of strains is negligible. In the case of $\rho\eta_0/b=O(\mathbf{e})$ the kinetics of transformation depends essentially on the solid properties.

ONE - DIMENSIONAL CONTINUUM

Cylindrical bar is further considered as an illustrative example. Material of the bar can be in a two-phase state. We suppose that the relative difference of elastic modules is negligible. The elastic potentials w_i and the Hook's law for initial and forming phases are given by expressions

$$w_1(e) = \tfrac{1}{2}Ee^2, \quad w_2(e) = \tfrac{1}{2}Ee^2 - Ee_0 e, \quad w_{pt}^0 = w_0 + \tfrac{1}{2}Ee_0^2, \quad \sigma_1(e) = Ee, \quad \sigma_2(e) = E(e - e_0) \tag{6}$$

Here E is the Young's module, w_{pt}^0 is latent energy, e_0 is own deformation of transition. The relations (1)-(2) on interface are reduced to the stress continuity $\sigma_1 = \sigma_2$ and a relation $w_2 - w_1 = \sigma_1(e_2 - e_1) - \delta_*$ for jump of energy. It gives

$$e_1 = (w_0 + \delta_*)/\sigma_0, \quad e_2 = e_1 + e_0, \quad \sigma^{(12)} = (w_0 + \delta_*)/e_0, \quad \sigma_0 \equiv Ee_0 \tag{7}$$

where $\sigma^{(12)}$ is a stress of *direct phase transition*. At *backward transition* we have

$$\sigma^{(21)} = (w_0 - \delta_*)/e_0 \tag{8}$$

From (7) and (8) it follows that hysteresis of phase transition in elastic bar $(\sigma^{(12)} - \sigma^{(21)})e_0 = 2\delta_*$.

Let's consider now this problem by kinetic model. According to (3), (6) we choose the elastic potentials of mixture

$$w(\mathbf{e}, \omega) = \frac{b}{n+1}\omega^{n+1} + g\omega + \tfrac{1}{2}(1-\omega)Ee^2 + \tfrac{1}{2}\omega(Ee^2 - 2\sigma_0 e), \qquad \sigma_0 \equiv Ee_0 \tag{9}$$

The kinetic equation (5) is written as $\dot{\omega} + \beta\omega^n = \beta b^{-1}(\sigma_0 e - g)$. The stress is expressed by formula $\sigma(e, \omega) = Ee - \sigma_0\omega$. For a *slow stretching* $e(t) = e_* + e_0 z(t)$, $z(0)=0$, $\tau\dot{z}(t) << 1$ the threshold deformation, when the phase transformation begins, $e_* = g/\sigma_0$, the structural parameter $\omega^n(t) = b^{-1}\sigma_0 e_0 z(t)$. The final deformation e_{**} corresponding to $\omega = 1$ is determined by equation $b^{-1}\sigma_0(e_{**} - e_*) = 1$. To express the quantities b, g through material parameters E, e_0, w_0 and to determine the dissipation δ_* we use the relations $e_* = e_1$, $e_{**} = e_2$, $b/(n+1) + g = w_0 + \tfrac{1}{2}\sigma_0 e_0$. In view of (7) we find

$$b = \sigma_0 e_0, \qquad g = u_0 - \sigma_0 e_0\,(1/2 - 1/(n+1)), \qquad \delta_* = \sigma_0 e_0\,(1/2 - 1/(n+1)).$$

From here it follows, that the singular source of dissipation is *uniquely connected to parameter n of kinetic equation*. The approximation of the reversible phase transition ($\delta_* = 0$) which was used in [1,3] within the framework of our model leads to the necessary usage of the linear kinetics (n=1). The non-zero dissipation ($\delta_* > 0$) corresponds to $n > 1$.

For linear kinetics at small strain rate the stress $\bar{\sigma}(t)$ expressed by relation $(\bar{\sigma} - Ee_*)/\sigma_0 = z(t) - z^{1/n}(t)$ approaches the value Ee_*. This value is appropriate to the model of quasistatic transition with a surface of strong discontinuity. For non-linear kinetics (n>1) the falling stress – strain dependence is typical. Amplitude and a negative inclination grow with an increase in a parameter n and a decrease in the strain rate. High-speed deformation ($\tau\dot{z}(t) >> 1$) is accompanied by monotonous growth of stress at all n. The large kinetic parameter is preferable, as in this case the transition from one branch on another is close to horizontal curve. It allows to speak about a stress which is characteristic for high-speed phase transition.

CONCLUSIONS

Thus, the offered kinetic model of phase transitions in thermoelastic solids satisfies to the following requirements:
- non-negativity of dissipation of structural transformation in any processes of thermal and mechanical loading;
- thermomechanical threshold, which overshoot is accompanied by the formation of new phase inclusions. Threshold is not an additional assumption, it follows from thermoelastic properties of a material;
- thermomechanical limit that corresponds to complete phase transition. As well as threshold, the limit is determined by thermal and mechanical characteristics of a material;
- strong interrelation of kinetics with thermodynamic potentials, which reflects the dependence of generation and growth of the new phase nucleolus from modules of both phases;
- dependence of the phase transition character (reversibility and irreversibility) from a kinetic parameter.

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