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Kinetics of phase boundaries and chemical reaction fronts in deformable solids

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We develop an approach to studying the influence of stresses and strains on the kinetics of phase boundaries or chemical reaction fronts based on the expression of the chemical affinity tensor that determines the configurational (driving, thermodynamic) force acting at the transformation front. We start with the consideration of a chemical reaction between solid and gas constituents

$$n_-B_- + n_*B_* \rightarrow n_+B_+$$

where B_-, B_* and B_+ are the chemical formulae of an initial solid constituent, a gas constituent and a transformed solid constituent, respectively, $n_\pm$ and n_* are stoichiometric coefficients. The reaction is localized at the reaction front and sustained by the diffusion of the gas through the transformed material. The reaction produces transformation strains and, thus, stresses which in turn, together with external loading, affect the reaction. It was shown (see [1, 2, 3] and reference therein) that the expression for the energy dissipation per unit area of the chemical reaction front takes the form

$$D = A_{NN}\omega_N = \frac{\rho_-}{n_-M_-}A_{NN}W_N \tag{1}$$

where ω_N is the reaction rate at the surface element with the normal $\mathbf{N}$, W_N is the transformation front velocity, ρ_- and M_- are the mass density and molar mass of an initial material B_-, $A_{NN} = \mathbf{N}\cdot\mathbf{A}\cdot\mathbf{N}$ is the normal component of the chemical affinity tensor $\mathbf{A}$. In a quasi-static case the chemical affinity tensor takes the form of the combination of chemical potentials tensors $\mathbf{M}_\pm = \mathbf{b}_\pm/\rho_\pm$ of the solid constituents equal to the Eshelby energy-momentum tensors $\mathbf{b}_\pm$ determined with respect to the stress-free configurations of the solid constituents $B_\pm$ and divided by the reference mass densities $\rho_\pm$ of initial and transformed solid constituents, and the chemical potential μ_* of the gaseous constituent:

$$\mathbf{A} = n_-M_-\mathbf{M}_- + n_*M_*\mu_*\mathbf{I} - n_+M_+\mathbf{M}_+ \tag{2}$$

where $\mathbf{I}$ is the unit tensor, M_+ and M_* are the molar masses of a transformed solid B_+ and gaseous B_* constituents. Additional terms appear in the dynamical case.

In the case of a phase transformation $n_* = 0$, $n_- = n_+ = 1$, $M_+ = M_- \equiv M$, $\mathbf{A} = M[\![\mathbf{M}]\!]$ where brackets denote a jump of a value, $[\![\,\cdot\,]\!] = (\,\cdot\,)_+ - (\,\cdot\,)_-$. The formula (1) becomes a known formula (see, e.g. [4]) for the dissipation due to the propagation of the phase boundary

$$D = -\mathbf{N}\cdot[\![\mathbf{b}]\!]\cdot\mathbf{N}W_N \tag{3}$$

where $[\![\mathbf{b}]\!] = \mathbf{b}_+ - \mathbf{b}_-$ is the jump of the Eshelby energy-momentum tensor $\mathbf{b}$ (see details in [3]).

We formulate kinetic equations as the dependencies of the transformation front velocity on the normal component of the jump of the Eshelby tensor in the case of moving interface (see, e.g., [5]) or the normal component of the affinity tensor in the case of propagating chemical reaction front. Then stresses and strains affect the transformation front velocity via the configurational force, in accordance with expressions obtained.

One can derive in the case of small strains, neglecting the input of the pressure into stresses, that

$$A_{NN} = \frac{n_- M_-}{\rho_-}\left(w_- - g^3 w_+ + \sigma_- : [\![\varepsilon]\!]\right) + n_* M_* \mu_*, \tag{4}$$

where $w_\pm$ are the Helmholtz free energies of the solid constituents per unit their reference volumes, σ_- is the Cauchy stress, $[\![\varepsilon]\!] = \varepsilon_+ - \varepsilon_-$, $\varepsilon_\pm$ are the strains, $g^3 = (n_+ M_+ \rho_-)/(n_- M_- \rho_+)$ relates the corresponding volume elements $dV_- = n_- M_- / \rho_-$ and $dV_+ = n_+ M_+ / \rho_+$ of the material B_- the material B_+ where ρ_+ is the mass densities of the material B_+ in a stress-free state [2]. For the simplicity sake we take μ_* in a form

$$M_* \mu_* = \eta_*(T) + RT \ln(c/c_*)$$

where R is the universal gas constant, c is the molar concentration of the gas constituent that is to be found from the diffusion problem, c_* and $\eta_*(T)$ are referential molar gas concentration and molar chemical potential (we assume that c_* is the gas solubility in the transformed material).

In the case of phase boundary the configurational force becomes $-\mathbf{N} \cdot [\![\mathbf{b}]\!] \cdot \mathbf{N} = -([\![w]\!] - \sigma_- : [\![\varepsilon]\!])$. In both cases the configurational force can be expressed via stresses or strains on one side of the transformation front (see, e.g., [7]).

We start with considering a planar transformation front propagation for linear elastic solid constituents. In the case of phase transformations we generalize the concept of phase transition zones (see [6] and reference therein) and construct the modified phase transition zones formed by all strains which can exist at the moving interface. This allows us to establish relationships between the strains at the moving interface and the interface orientation and velocity. Then we study how inelastic strains affect the interface propagation considering simplest5 boundary value problems. After that we generalize the consideration for the case of a propagating chemical reaction front and present solutions of a number of problems of mechanochemistry for elastic and inelastic solids. Having in mind experimental data (see, e.g., [8]) we study how stress relaxation due to viscosity and plasticity affects the transformation front propagation. We show how stresses can accelerate, retard and even block the front propagation. On the whole, we demonstrate the variety of the transformation front behaviors in dependence on reaction parameters, rheological models chosen for the solid constituents, material parameters, external and internal stresses and temperature.

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