

## Kinetics of Phase Boundaries and Chemical Reaction Fronts in Deformable Solids

**A. Freidin**<sup>1,2,3</sup>, **N. Morozov**<sup>1,2</sup>,  
**L. Sharipova**<sup>1</sup>, and **E. Vilchevskaya**<sup>1,3</sup>

<sup>1</sup>Institute for Problems in  
Mechanical Engineering of the  
Russian Academy of Sciences,  
Bolshoy Pr., 61, V.O., St.  
Petersburg, 199178, Russia,  
alexander.freidin@gmail.com,  
morozov@nm1016.spb.edu,  
sleah@gmail.com,  
vilchevska@gmail.com

<sup>2</sup> St. Petersburg State University,  
Universitetsky Pr., 28, Peterhof, St.  
Petersburg 198504, Russia

<sup>3</sup> St. Petersburg Polytechnic  
University, Polytechnicheskaya Str.,  
29, St. Petersburg 195251, Russia  
alexander.freidin@gmail.com

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 configuration (driving, thermodynamic) force acting at the transformation front. We start from 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 the original solid constituent, the gas constituent, and the transformed solid constituent, respectively, and  $n_+$  and  $n_*$  are the 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 hence stresses, which, in turn, together with external loading, affect the reaction. It was shown (see [1, 2, 3] and references therein) that the expression for the energy dissipation per unit area of the chemical reaction front takes the form

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

where  $\omega_N$  is the reaction rate at the surface element with normal  $\mathbf{N}$ ,  $W_N$  is the transformation front velocity,  $\rho_-$  and  $M_-$  are the mass

density and molar mass of the original material  $B_-$ , and  $A_{NN} = \mathbf{N} \cdot \mathbf{A} \cdot \mathbf{N}$  is the normal component of the chemical affinity tensor  $\mathbf{A}$ . In the quasi-static case, the chemical affinity tensor takes the form of a combination of the chemical potential tensors  $\mathbf{M}_\pm = \mathbf{b}_\pm / \rho_\pm$  of the solid constituents, which are equal to the Eshelby energy–momentum tensors  $\mathbf{b}_\pm$  determined with respect to the stress-free configurations of the solid constituents  $B_\pm$  divided by the reference mass densities  $\rho_\pm$  of the original and transformed solid constituents, and the chemical potential  $\mu_*$  of the gaseous constituent,

$$\mathbf{A} = n_- M_- \mathbf{M}_- + n_* M_* \mu_* \mathbf{I} - n_+ M_+ \mathbf{M}_+, \quad (2)$$

where  $\mathbf{I}$  is the unit tensor and  $M_+$  and  $M_*$  are the molar masses of the transformed solid  $B_+$  and gaseous  $B_*$  constituents. Additional terms appear in the dynamic 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 in a value,  $[[\cdot]] = (\cdot)_+ - (\cdot)_-$ . Formula (1) becomes a known formula (e.g., see [4]) for the dissipation due to the propagation of the phase boundary,

$$D = - \mathbf{N} \cdot [[\mathbf{b}]] \cdot \mathbf{N} W_N, \quad (3)$$

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 (e.g., see [5]) or the normal component of the affinity tensor in the case of a propagating chemical reaction front. Then the stresses and strains affect the transformation front velocity via the configurational force, in accordance with the expressions obtained.

In the case of small strains, neglecting the input of the pressure into stresses, one has

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

where the  $w_{\pm}$  are the Helmholtz free energies of the solid constituents per unit reference volumes,  $\sigma_-$  is the Cauchy stress,  $[[\varepsilon]] = \varepsilon_+ - \varepsilon_-$ , the  $\varepsilon_{\pm}$  are the strains, and  $g^3 = (n_+ M_+ \rho_-)/(n_- M_- \rho_+)$  relates the corresponding volume elements  $dV_- = n_- M_-/\rho_-$  and  $dV_+ = n_+ M_+/\rho_+$  of the material  $B_-$  and the material  $B_+$ , where  $\rho_+$  is the mass density of the material  $B_+$  in a stress-free state [2]. For simplicity, we take  $\mu_*$  in the 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 to be found from the diffusion problem, and  $c_*$  and  $\eta_*(T)$  are the referential molar gas concentration and the molar chemical potential. (We assume that  $c_*$  is the gas solubility in the transformed material.)

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

We start from 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 references therein) and construct 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 the simplest five 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 (e.g., see [8]) we study how the stress relaxation due to viscosity and plasticity affects the

transformation front propagation. We show how the stresses can accelerate, retard, and even block the front propagation. Overall, we demonstrate a variety of transformation front behaviors in dependence on reaction parameters, rheological models chosen for the solid constituents, material parameters, external and internal stresses, and temperature.

This reserach was supported by the Russian Foundation for Basic Research (Grant No. 13-01-00687).

## References

- [1] *A. B. Freidin*. Chemical affinity tensor and stress-assist chemical reactions front propagation in solids. ASME 2013 International Mechanical Engineering Congress and Exposition, V. 9: Mechanics of Solids, Structures and Fluids. San Diego, California, USA, Paper No. IMECE2013-64957, V009T10A102. 2013.
- [2] *A. B. Freidin, E. N. Vilchevskaya, and I. K. Korolev*. Stress-assist chemical reactions front propagation in deformable solids. International Journal of Engineering Science. Vol. 83, pp. 57–75. 2014.
- [3] *A. B. Freidin*. On a chemical affinity tensor for chemical reactions in deformable solids. Mechanics of Solids. Vol. 50. No. 1. 2015.
- [4] *K. Wilmski*. Thermomechanics of Continua. Berlin, etc. Springer, 1998. 273 p.
- [5] *R. Abeyaratne and J. K. Knowles*. Elovution of Phase Transformation. A Continuum Theory. Cambridge University Press, 2006. 241 p.
- [6] *A. B. Freidin and L. L. Sharipova*. On a model of heterogenous deformation of elastic bodies by the mechanism of multiple appearance of new phase layers. Meccanica. Vol. 41, pp. 321–339. 2006.
- [7] *A. B. Freidin*. On new phase inclusions in elastic solids. ZAMM. Vol. 87(2), pp. 102-116. 2007.
- [8] *C. C. Buttner and M. Zacharias*. Retarded oxidation of Si nanowires. Applied Phys. Lett. Vol. 89, 263106, 2006.