

A kinetic model for anisotropic reactions in amorphous solids



Wei Hong

Department of Aerospace Engineering, Iowa State University, Ames, IA 50011, USA

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ABSTRACT

When mechanical constraints are present, solid-state reactions often induce deviatoric inelastic strains in addition to volume change. Existing models either attribute such deformation to the plastic flow driven by the stress exceeding a non-measurable kinetic-dependent yield strength, or need to introduce a deviatoric-stress-dependent chemical potential. By employing the transformation strain to characterize the state of reaction, this letter formulates a kinetic model via averaging the reaction rate at all possible orientations. The model is illustrated through the constrained lithiation–delithiation process of silicon as an example. With just one fitting parameter, the model can quantitatively capture the experimental results. The model only hypothesizes linear kinetics, and does not need to introduce kinetic-dependent plasticity or modify basic thermodynamic quantities. This approach can also be applied to other material systems, as well as extended to the nonlinear kinetics of far-from-equilibrium reactions.

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Solid-state reactions are seldom regarded a new topic in material synthesis, but when it comes to the strains or stresses induced by reactions, little has been explored beyond the similarities with liquid- or gas-state reactions. With the acceptance of another reactant through diffusion or other means of transportation, a solid reactant may expand in volume and/or change in shape. The common approach of modeling such processes is to assign a stress- and kinetics-independent transformation strain to the resultant. [1–4] The actual state of deformation is then calculated based on linear elasticity (or elasto-plasticity) as if the stress was applied after the reaction. Such a decoupled approach may be applicable to a reaction of which a transformation strain is clearly defined, e.g. one with a background crystalline reactant that retains its coherency throughout the process, as sketched in Fig. 1(a). However, this approach may be problematic if either the reactant or the resultant is amorphous, and thus the transformation strain or its orientation cannot be uniquely determined by the state of reaction. As illustrated by Fig. 1(b), without

significantly rearranging the spatial distribution of the reactant atoms, the resultants can bear very different transformation strains, depending on the relative positions of the inserted atoms. Variants of the resultants as those sketched in Fig. 1(b) are chemically identical, but mechanically different if the material is stressed or constrained.

To model the deformation involved in such reactions, it has been assumed that the transformation strain of an amorphous reaction is purely volumetric, and a separate process of plastic flow generates deviatoric inelastic strain, when the equivalent stress exceeds a threshold—the yield strength. However, the yield strength needs to be taken as composition and kinetics dependent. [3,4] Such an assumption is perhaps originated from the description of liquid reactions, in which the state of reaction can be fully described by a scalar variable. For solid reactants, the assumption is less convincing. The plentiful observations on reactions which transform crystalline solids into amorphous resultants [5–11], and complete within atomically sharp phase boundaries [12], may serve as counter evidences of this assumption: the amorphization would require plastic flow that is non-affine at atomic level which defies the applicability of continuum notions in the first

E-mail address: whong@iastate.edu.

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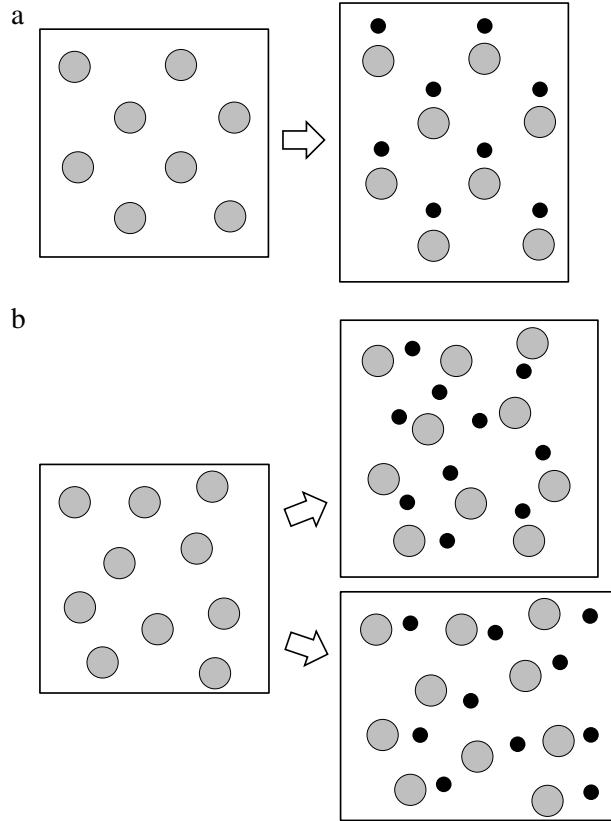


Fig. 1. Schematics of reaction-induced deformation. (a) For a coherent crystalline-to-crystalline reaction, the transformation strain is well-defined. (b) For an amorphous-to-amorphous reaction, the deviatoric strain is arbitrary from the chemical consideration only—with the same relative positions and average atomic distances, the resultants may differ by a deviatoric strain.

place. It is natural to believe that such deformation takes place right at the insertion of the second reactant, instead of after the reaction.

The ambiguity could be clarified if one allows additional variables for the state of reaction. To differentiate between resultant variants like those sketched in Fig. 1(b), one needs a state variable which contains the orientation information. While the choice is more or less arbitrary, in this letter we select the transformation strain tensor \mathbf{e}^t as the state variable. The rate of the reaction, represented by the time derivative of the transformation strain, $\dot{\mathbf{e}}^t$, is a function of the electrochemical driving force for the reaction $\Delta\mu$ and the stress tensor $\boldsymbol{\sigma}$. To simplify representation, we further decompose $\dot{\mathbf{e}}^t$ into the volumetric and deviatoric parts:

$$\dot{\hat{\epsilon}}_{ij}^t = \frac{\dot{\epsilon}_v}{3} \delta_{ij} + \dot{\hat{\epsilon}}_{ij}^t. \quad (1)$$

Although the isotropy of the material requires the volumetric strain rate to be dependent only on the electrochemical driving force and the hydrostatic stress, the deviatoric strain rate $\dot{\hat{\epsilon}}^t$ could be dependent on the deviatoric stress $\tilde{\boldsymbol{\sigma}}$. In a simple case when the dependence is linear,

$$\dot{\hat{\epsilon}}_{ij}^t = T_{ijkl} \tilde{\sigma}_{kl}, \quad (2)$$

where \mathbf{T} is a fourth rank tensor relating the two deviatoric tensors, and the repeated indices indicate a summation. The isotropy of the amorphous material requires \mathbf{T} to contain only one scalar parameter ν , and the transformation strain rate to be parallel to the stress deviator:

$$\dot{\hat{\epsilon}}_{ij}^t = \nu \tilde{\sigma}_{ij}. \quad (3)$$

Although the kinetic relation (3) shares the same form as that of a Newtonian fluid, here ν is not a material constant, and could be dependent on the concentration of the mobile reactant or the energetic driving force. Instead of driven by shear stresses as a viscous fluid, the transformation strain should be regarded as a part of the reaction process, and is nonzero only when the reaction is taking place. It should be noted that relations in the form of Eq. (3) also appear in most existing theories of related phenomena, [1,3,4,13] but the difference lies in the coefficient ν and the underlying physical interpretation. For example, the similar expression in the reactive flow theory is interpreted as the plastic flow driven by a stress exceeding the yield strength. [1,2] In some other models, the reactant chemical potential needs to be modified to include a contribution from deviatoric stress, [13,14] and thus the scalar reaction rate (or volumetric strain rate) is also affected. In contrast to the existing theories, the current model makes no hypothesis other than linear kinetics and linear elasticity, as detailed in the following discussion.

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