



Stress-assist chemical reactions front propagation in deformable solids



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ABSTRACT

We consider a stress-assist chemical reaction front propagation in a deformable solid undergoing a localized chemical reaction between solid and gas constituents. The reaction is sustained by the diffusion of the gas constituent through the transformed solid material. The transformation strain produced by the chemical reaction lead to internal stresses which in turn affect the chemical reaction front kinetics. Basing on the notion of the chemical affinity tensor we formulate a kinetic equation in a form of the dependence of the front velocity on the normal component of the chemical affinity tensor. As an example we consider a planar chemical reaction front propagation in an elastic plate subjected to uniaxial tension or compression. We demonstrate the possibility of the locking effects – blocking the reaction by stresses at the reaction front. We study in details how the velocity of the chemical reaction front and the locking effect depend on chemical reaction parameters and external loading.

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1. Introduction

Interconnections between chemical reactions and deformation and fracture processes remain to be of significant interest for both fundamental and applied science. For example, silicon oxidation has played an important role in the development of silicon integrated-circuit technology. The stress-assist oxide layer growth in micronscale parts of MEMS made of polycrystalline silicon thin films determines the life time of MEMS (see details and reference in [Muhlstein & Ritchie \(2003\)](#)). Another example of motivations for detailed mechano-chemistry modeling is given by the processes of metal hydride formation used in hydrogen storage applications (see, e.g., [Kelly & Clemens, 2010](#); [Kikkinides, 2011](#)).

The silicon oxidation as well as hydrogen absorption are sustained by the diffusion of the gas constituent through the transformed material and the chemical reaction takes place at the chemical reaction front that divides two solid constituents. One of the first and more significant models describing such reactions was suggested by [Deal and Grove \(1965\)](#). This model was one-dimensional, stress free and applied for films growth on plane substrates.

Then it was realized that kinetics of oxide film grown on nonplanar substrates differs from oxide grown on planar substrates. Marcus and Sheng observed retarded oxide growth at both convex and concave corners of trenches in silicon ([Marcus & Sheng, 1982](#)). [Kao, McVitie, Nix, and Saraswat \(1985, 1987\)](#) performed a set of experiments in which the oxidation of

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cylindrical silicon structures was studied. It was demonstrated that the oxidation of curved silicon surfaces is retarded at sharp curvatures, and that the retardation is more severe on concave than convex structures. From these facts it has been inferred that internal stresses generated during the oxidation process affect the oxidation behavior.

The influence of external stresses was examined by Huang, Jaccodine, and Butler (1987). It was shown that external tensile stresses enhanced the oxidation rate, and compressive stresses retarded it. Another experimental tests were done by Mihalyi, Jaccodine, and Delph (1999) for silicon strips in four-point bending in oxidizing environment. The results of this set of experiments indicated that applied compressive stress had a retarding effect upon the growth of the oxide layer, while the effect of tensile stress was ambiguous. Meanwhile, Yen and Hwu (2000), studying the effect of external stress on oxidation of silicon wafers, showed that the tensile stress strongly enhances the oxidation rate.

To explain microscopic oxidation behavior a number of models have been developed by extending the Deal–Grove model to two-dimensional stress-dependent models (see e.g. Coffin et al., 2006; Delph, 1998; Kao et al., 1987; Kao, McVitie, Nix, & Saraswat, 1988; Rafferty, 1989; Rao & Hughes, 2000; Rao, Hughes, & Garikipati, 2000; Senez, Collard, Baccus, Brault, & Lebailly, 1994; Sutardja & Oldham, 1988; Tersoff, Tu, & Grinstein, 1998). To take into account stress effects, these models proposed stress dependent oxidation parameters: surface reaction rate, oxidant diffusivity, and oxide viscosity. First models assumed that the parameters were affected mostly by hydrostatic and normal stresses at the reaction front. Then models were elaborated with shear stress-dependent viscosity. The choice of the parameters of the models was justified by the agreement between theoretical results and experimental data on the oxidation kinetics.

Note that the dependencies of the parameters on stresses were introduced heuristically. In the present paper we try to describe the stress effect basing on the notion of chemical affinity. This notion was introduced by Gibbs (1948) and de Donde (1936) and laid the foundation of rational thermodynamic theory of phase transformations and chemical reactions. The expression of the chemical affinity was obtained as a combination of the chemical potentials of the substances (constituents) involved into the transformation. A kinetic equation was formulated that determined the reaction rate as a function of the chemical affinity acting as a thermodynamic force (see, e.g. Prigogine & Defay, 1988).

In the second part of the XX century it was realized that the phase equilibrium at the interphase boundary in a deformable solid depends on the orientation of the boundary with respect to stress and isotropy axes. This resulted in understanding that the chemical potential is to be a tensor in the case of solid phases. The derivations showed that the chemical potential tensor was equal to the Eshelby energy–momentum tensor (Eshelby, 1975) divided by the referential mass density, and phase equilibrium at the interphase boundary as well as the kinetics of the interface were determined by the normal components of chemical potential tensors of the phases (see, e.g., Abeyaratne & Knowles, 2006; Grinfeld, 1991 and references therein). Tensorial nature of the chemical potential and the chemical affinity also have been discussed in Rusanov (2005, 2006).

Then an expression of the chemical affinity tensor as a combination of Eshelby stress tensors of solid constituents and a chemical potential of a gas constituent was derived for the case of nonlinear elastic solid constituents (Freidin, 2009) and for arbitrary solid constituents (Freidin, 2013, 2014).

In the last case we wrote down the mass, momentum and energy balances for an open system in which a chemical reaction took place between diffusive gas constituent and a solid with arbitrary constitutive equations. Then the expression of the entropy production due to the reaction front propagation in a solid with arbitrary constitutive equations was derived. It was shown that the chemical affinity tensor determined the configurational force that drove the propagation of the reaction front. The tensorial nature of the chemical affinity was explained by the fact that one should consider the reaction rate at oriented surface elements in the case of a deformable solid and the reaction rate depended on the orientation of the surface element with respect to stress axes – in contrast to the volume reaction rate in classical physical chemistry conjugated to a scalar chemical affinity in the expression of the entropy production (cf. with Loeffel & Anand (2011) and Loeffel, Anand, & Gaseem (2013) where a coupled chemo-mechanical theory for elastic-viscoplastic deformation, diffusion, and volumetric swelling due to a chemical reaction was developed for a volume-distributed reaction).

Basing on the notion of the chemical affinity tensor we considered axially-symmetric problems of mechanochemistry: the oxidation of an elastic cylinder and an infinite body with a cylindrical hole (Vilchevskaya & Freidin, 2013), where the dependence of the reaction kinetics on the surface curvature was demonstrated. In the present paper we solve the simplest boundary value problem – the chemical reaction front propagation in an elastic plate.

We start with the description of the reaction between the gas and arbitrary solid constituent in a case of finite strains. In Section 2 we describe the configurations produced by chemical reactions and deformations and determine the chemical transformations strain tensor. In Section 3 we write down the expression of the chemical affinity tensor. In Section 4 we formulate a kinetic equation that determines the reaction front velocity in dependence on the normal component of the chemical affinity tensor that, in turn, depends not only on the reaction parameters and temperature but also on stresses at the reaction front.

Following Vilchevskaya and Freidin (2009, 2010, 2013) we introduce the notion of the equilibrium gas concentration as the concentration at which the normal component of the chemical affinity is zero and then reformulate the kinetic equation in terms of current gas concentration at the reaction front and equilibrium concentration that depends on stresses at the front. We note that if the equilibrium concentration at the reaction front is greater than the concentration at the outer surface of the body then the front propagation is impossible. This means the possibility of the locking effects – blocking the reaction by stresses at the reaction front.

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