ON KINETICS OF CHEMICAL REACTIONS FRONTS IN ELASTIC SOLIDS

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Summary A chemical reaction of the oxidizing type is considered. It is shown that strains produced by the chemical reaction lead to internal stresses at the reaction front which in turn affect the chemical reactions front kinetics. We discuss how external and internal stresses can accelerate or decelerate the reaction front propagation (including locking effect).

STATEMENT OF THE PROBLEM

Interrelations between kinetics of chemical reaction and a mechanical state of a body are of significant interest for both fundamental and applied engineering science. Chemomechanical problems have received a new attention in recent years due to miniaturization of structure elements. For example, micron-scale polycrystalline silicon thin films are widely used in MEMS. As it was established in [1], a mechanism associated with failure of the films involves sequential oxidation and environmentally-assisted crack grows solely within SiO_2 layer, which kinetic is determined by mechanical stresses. A thin surface oxide layer may also play a protected role, but its damage or additional loading leads to further chemical reactions.

We consider a stress-assist chemical reaction front propagation implying the reaction like the silicon oxidation within the frameworks of configuration (driving) forces concept. We suppose that the reaction is localized at the front that divides two solid constituents and sustained and controlled by the diffusion of the gas constituent through the transformed material. We also assume that the gas diffusion is not affected by strains and does not produce additional strains in the solid phases.

We obtain an expression of the entropy production due to the reaction front propagation and, as a result, derive the formula of the chemical affinity tensor as a combination of Eshelby stress tensors of the solid constituents and a chemical potential of a gas constituent. In a linear thermodynamic approach a velocity of the reaction front is proportional to a normal component of the chemical affinity tensor which depends on stresses and the gas constituent concentration. We say that the gas concentration is equilibrium c_{eq} at the reaction front if, given temperature, front position and stresses, the normal component of the chemical affinity is equal to zero. Since the concentration c_{eq} depends on stresses, the stresses can accelerate or lock the reaction front propagation.

An axially-symmetric mechano-chemistry problem is considered as a model problem. Given transformation strain we show that in the absence of external stresses the reaction rate in the case of a convex surface is greater than in the case of non-convex surface. At the same time the oxide layer growth leads to the equilibrium concentration increase in the case of the convex surface, which in turn may lock the reaction. External pressure applied can make the reaction possible at all thicknesses of oxide layer but further pressure increase may lead to total locking of the reaction. This effect is a consequence of the non-monotonic dependence of c_{eq} on pressure. In contrast, in the case of non-convex surface, the oxide layer growth decreases the equilibrium concentration that in turn facilitates the chemical reaction front propagation.

FEM-SIMULATION

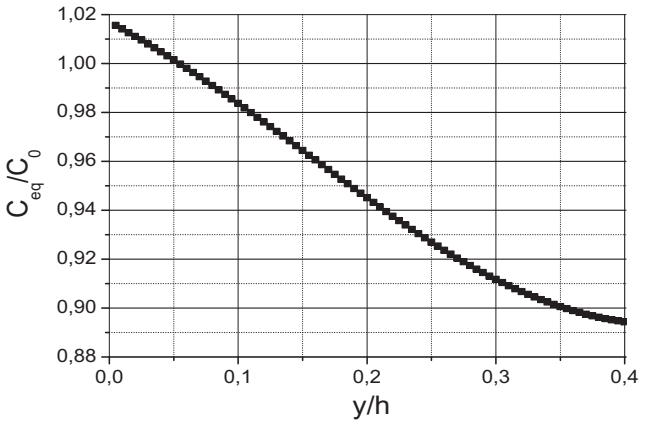

Figure 1. The dependence of c_{eq}/c_0 on the relative layer thickness y/h, h – the specimen height, y – the layer thickness

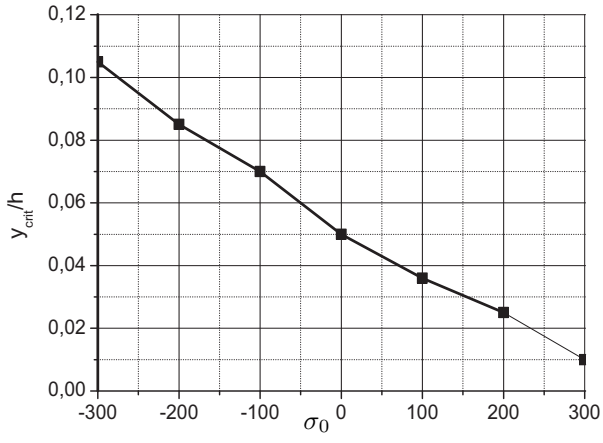

Figure 2. The dependence of the critical layer thickness on external stress

FEM-model for the chemical reaction front propagation in elastic solids is elaborated. We start with FEM-simulation of the plane oxide layer growth. If the external stress is zero then, given the gas outer concentration c_0 and the temperature,

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internal stresses produced by the reaction can lock the reaction if the oxide layer thickness is less then a critical value. The critical thickness can be estimated as a thickness at which $c_{eq}/c_0 = 1$ (See Fig. 1). External stress σ_0 acting along the reaction front changes the critical thickness. The critical thickness increases in the case of compression and decreases in the case of tension (Fig. 2). Thus, even if the reaction was locked due to the thin protecting layer existence, tension may initiate further chemical reaction. In contrast to tension, compression may decelerate or lock the front propagation. This means, for example, that in a case of a bending plate the reaction may take place at the stretching side and may be locked at the compressed side.

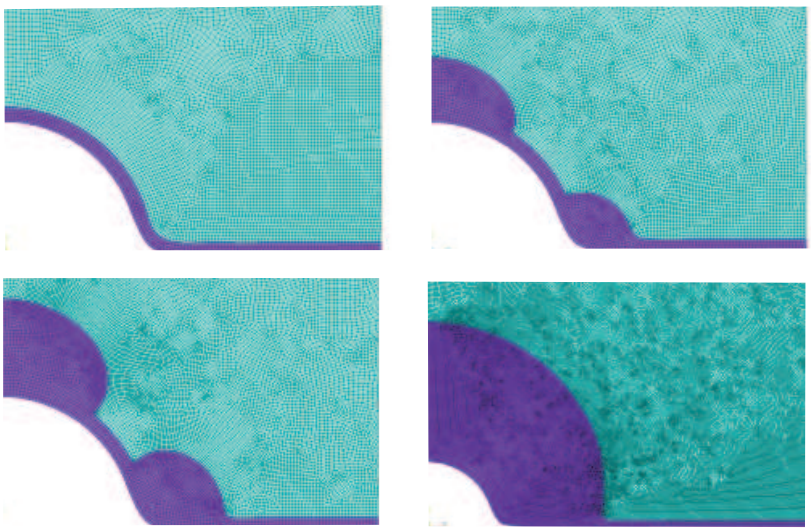

Figure 3. Oxide zone evolution in a specimen with a groove.

An example of FEM-simulation of the chemical reaction front propagation in a specimen with a semi-circular groove is shown in Fig. 3.

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References

[1] C.L. Muhlstein, E.A. Stach, R.O. Ritchie: A reaction-layer mechanism for the delayed failure of micron-scale polycrystalline silicon structural films subjected to high-cycle fatigue loading. *J. Acta Materialia* **50**:3579Ű-3595, 2002.