A New Numerical Formulation for Thermal Oxidation

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Abstract— A new numerical formulation to model oxidation is proposed. It includes discontinuous shape functions to model two material diffusion-reaction, level-set based interface evolution, viscoelastic constitutive relations, finite deformation and large expansion. Well-posedness and numerical stability of the numerical methods are investigated in detail. Stressdependent oxidation and residual stresses can be treated in one, two and three dimensions. Traditional gridding problems associated with moving boundaries are resolved by using an Eulerian representation of the interface. The constitutive model is thermodynamically consistent and preserves fundamental properties like objectivity of constitutive equations throughout the process.

I. INTRODUCTION

Thermal oxidation, at a process modeling level, can be looked at as a three step coupled process. The steps are, (i) reaction of Si and O_2 to form SiO₂, (ii) diffusion of O_2 through SiO₂ and (iii) the mechanical equilibration following the expansion associated with the reaction in step (i). In reality, these processes are happening simultaneously. For simulation purposes, a mathematical model is required. This would, typically, be a system of differential equations. These can be obtained by investigating the fundamental balance laws of mass, momentum and energy. In the following sections, equations governing the three steps will be derived and their numerical implementation will be described.

II. OXIDANT DIFFUSION

The transport theorem is the fundamental equation from which all the balance laws can be derived. If the integrand is chosen to be the density, one gets the mass balance equation. Similar equations can be derived for momentum and energy balance. For the diffusion problem, density of the oxidant is used as the field variable in the transport equation. The presence of a reaction surface

Grant No. ARMY DABT 63-93-C-0053

is taken into account by incorporating jumps in the field variable (and, therefore, the flux computations). This is a departure from traditional diffusion modeling mechanisms. The transport equation for conservation of mass with surface of discontinuity, Γ is given by

$$\frac{\mathrm{d}}{\mathrm{d}t} \int_{\Omega} \rho \,\mathrm{d}\Omega = \int_{\Omega} \frac{\partial \rho}{\partial t} \,\mathrm{d}\Omega + \int_{\partial \Omega} \rho \,\mathbf{v} \cdot \mathbf{n} \mathrm{d}\Gamma - \int_{\Gamma} \left[\! \left[\rho \right] \! \right] V_n \,\mathrm{d}\Gamma.$$
(1)

In the above equation, ρ is the density of the diffusing species and V_n is the speed of the discontinuity surface. The direction of motion of the surface is given by **n**, normal to the surface of discontinuity and $\llbracket \cdot \rrbracket$ is the symbol representing jump in the argument.

This equation incorporates all the possible modes in which the oxidant can be transported through a medium. The increase in mass (due to the oxidant diffusing *into* the medium from the SiO_2-O_2 interface) is taken into account with a boundary flux term. Divergence theorem yields the diffusion term.

Applying the assumption that the process is slow and in the absence of convection, global conservation provides the generalization of the Deal-Grove model in multiple dimensions.

$$\int_{\Omega} \nabla \cdot \mathbf{F} \, \mathrm{d}\Omega = \int_{\Gamma} \left[\!\!\left[\mathbf{F} \cdot \mathbf{n}\right]\!\!\right] \mathrm{d}\Gamma - \int_{\Gamma} \left[\!\!\left[\rho\right]\!\right] V_n \, \mathrm{d}\Gamma \quad (2)$$

Where, $\mathbf{F} = -D \frac{\partial \rho}{\partial \mathbf{x}}$ is the diffusive flux and $[\![\mathbf{F} \cdot \mathbf{n}]\!] = k_s \rho^-$ represents the reaction term.

Note, standard Galerkin techniques using piecewise continuous shape functions (C^0 continuous) cannot be used to numerically approximate equation [2]. This will be dealt with *enhanced* finite element methods.

Well-posedness of the diffusion equation requires one more condition at the interface. This is given by the segregation condition.

Manuscript received March 3, 1997.

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A. Weak Form of Diffusion Equation

Using the notation in [2],

$$(\nabla v, \mathbf{F})_{\Omega^{-} \cup \Omega^{+}} - (v, \llbracket \mathbf{F} \cdot \mathbf{n} \rrbracket)_{\Gamma} + (v, \llbracket \rho \rrbracket V_{n})_{\Gamma} - (v, \mathbf{F} \cdot \mathbf{n})_{\partial \Omega} = 0$$
 (3)

Standard piecewise linear shape functions can be used to approximate the concentration field in all regions except near Γ . Across the surface of discontinuity, continuous interpolations are enhanced with discontinuous interpolations that are zero at the vertices. Jump in concentration and fluxes provide the two equations to determine the exact topology of the shape function. For one and two dimensions they are shown in figure [1]. Location of the jump within an element is to be determined separately. This will be explained in section III.

The enhancements are designed such that they are discontinuous across adjacent elements. This uncouples the unknowns determining the jump heights. They can thus be computed within the element and the need for global assembly in obviated. The enhancements are stable and convergent. Their theory is described in [1] and references therein.

III. SURFACE EVOLUTION

The level-set method [5] is used to describe surface evolution. It is robust and allows easy extension to three dimensions.

The Si-SiO₂ boundary is described as the zero level set of a higher dimensional surface. Evolution of this surface can be described by a non-linear advection equation. This provides for an easy description of complicated surfaces in addition to the rich mathematical theory that comes under the Hamilton–Jabobi equations.

The non-linear advection equation for the level-set function ψ is given by,

$$\frac{\partial \psi}{\partial t} + F_n \|\nabla \psi\| = 0. \tag{4}$$

The L_2 norm is given by $\|\cdot\|$. F_n is the speed of the propagating surface. Note, the equation is non-linear in two or higher dimensions.

The reason for calling equation [4] as an advection equation becomes clear when the spatial term is written as

$$F_n \|\nabla\psi\| = F_n \frac{\nabla\psi}{\|\nabla\psi\|} \cdot \nabla\psi \tag{5}$$

Defining $\mathbf{a} = F_n \nabla \psi / ||\nabla \psi||$, a purely advective system is obtained. Non-linearity arises out of dependence of \mathbf{a} on $\nabla \psi$.

A. Numerical Formulation

Assuming appropriate topologies for the trial and weighting function spaces the semi-discrete weak form of equation [4] is written as,

$$(w,\psi_t) + (w, \boldsymbol{a} \cdot \nabla \psi) = 0 \tag{6}$$

where, $\mathbf{a} = F_n \nabla \psi / ||\nabla \psi||$, is the advection velocity.

It is well-known that pure advection equations are spatially unstable. Standard procedures to stabilize these equations are upwinding and artificial diffusion. Both these methods introduce diffusion like terms in the equation to provide spatial stability. In the finite element literature, Galerkin least squares method, suggested by Hughes [3] and co-workers in the context of fluid dynamics is widely used. The stabilized equation is given by,

$$(w,\phi,t) + a(w,\phi) + (\mathcal{L}w,\tau \mathcal{R}(\phi)) = (w,f)$$

where, \mathcal{L} is the spatial differential operator and \mathcal{R} is the residual. Making the least squares term residual dependent is crucial in rendering the formulation consistent. As the exact solution is approached the residual \mathcal{R} tends to zero and the original equation is obtained. The least squares term is defined only in element interiors in case C^0 interpolations are used. The design parameter τ is chosen to provide exactness in one dimension. This, of course, is not the only choice. For the problems in this work, it worked well.

Time integration of the advection equation is performed using the forward-Euler scheme. The scheme is explicit if the mass matrix is lumped. A further advantage of explicit scheme is that no non-linear solves are required. But, explicit schemes are first order accurate and conditionally stable. First order accuracy implies, the error reduces to zero linearly with the time step Δt . Conditional stability implies the existence of upper bound on the time step Δt . Clearly, there is a tradeoff between unconditionally stable methods (always implicit) and explicit methods.

IV. MECHANICAL PROBLEM

The quasistatic conservation of momentum provides the equations for the stress problem. Finite deformation kinematics release the constraint that deformations be small perturbations about the original configuration. Theoretical aspects of the formulation are drawn from the mathematical theory of elasticity [6]. The equations for mechanical equilibrium are given by

$$\nabla \cdot \boldsymbol{\sigma} = 0 \tag{7}$$

where, σ is the Cauchy stress tensor. The above equations are written in the current configuration. The implication is that the derivatives are computed with respect to the current placement. The field variables are the displacements. Strain measures can be defined in both current and reference configurations. Strains are functions of the displacements. Stresses are computed from strains using constitutive laws. The constitutive laws define material behavior. It is well known that the oxide behaves like a viscoelastic solid. In the remaining part of this section a viscoelastic constitutive model is developed. The model will be developed entirely in the reference configuration to ensure objectivity (material frame indifference).

Define *Helmholtz* free energy by

$$\Psi = U(J) + \bar{\Psi}(\bar{E}) - Q : \bar{E}$$
(8)

where, E is the Lagrangian strain and J is the determinant of Jacobian of the transformation (deformation gradient). Internal variables Q are introduced in constitutive theories to model dissipation. The first two terms define the elastic part of the free energy. This is the part of the energy that can be recovered (reversible) during unloading. It is also referred to as the stored energy. The functional form of the elastic part is decided based on the molecular structure of the material and kinematical constraints. In addition to the free energy, evolution equations are prescribed to fully define the internal variables. Restrictions on internal variables and the boundary conditions for the evolution equations arise out of thermodynamics. Viscoelastic behavior is defined by the following evolution equation for Q, see [7].

$$\dot{Q} + rac{Q}{\eta} = rac{1}{\eta} \left(\mathrm{DEV} \left[rac{\partial ar{\Psi}}{\partial ar{E}}
ight]
ight)$$

where, η is the relaxation time. The internal variable is a purely deviatoric quantity. Given the incompressibility of SiO₂ volume changes are absent. Hence, there can be no volumetric dissipation.

In the limit, free energy should reach steady state. This is a thermodynamic necessity. A material cannot dissipate for infinite time. Also, the dissipation cannot be less than zero. This implies an increase in the internal energy of the system. The latter is a statement of the second law of thermodynamics.

Solution to equation [9] can be written as a convolution integral. Convolution integrals are hard for numerical implementation. They require complete time history of the integrand. Instead, following [7] a two point recurrence relation can be used.

The recurrence formula is derived as follows. Consider the following convolution integral.

$$\boldsymbol{h}(t) = \int_0^t \exp\left[\frac{s-t}{\tau}\right] \frac{\mathrm{d}}{\mathrm{d}s} \boldsymbol{q} \,\mathrm{d}s \tag{9}$$

Using $h_{n+1} = h(t_{n+1})$, $h_n = h(t_n)$, applying mid-point rule to the time derivative term inside the integral and integrating, we get,

$$\boldsymbol{h}_{n+1} = \boldsymbol{h}_n \exp\left[\frac{-\Delta t}{\tau}\right] + \exp\left[\frac{-\Delta t}{2\tau}\right] \{\boldsymbol{q}_{n+1} - \boldsymbol{q}_n\} \quad (10)$$

It is now a two point recurrence relation. The data base requires one history term. The recurrence relation is based on the use of mid-point rule which renders it unconditionally stable and second order accurate. Again, the integration can be done entirely in the reference configuration thus trivially satisfying objectivity.

When the reaction between O_2 and Si takes place, silicon is consumed and SiO₂ is formed. Molar volume of SiO₂ is 2.2 times that of Si. So, the volume occupied by the newly formed SiO₂ is 2.2 times the volume of Si that was consumed. This phenomenon must be duplicated in the numerical framework and is described in the next subsection.

A. Large Expansion

During deformation, volume change is parameterized by the Jacobian of the gradient of the deformation. Intuitively, it can be looked at as the linearization of the deformation in a small neighborhood of the point of interest. Scalar triple product of the three axes associated with that point that form the basis, gives the volume. If the original set of axes were the usual Euclidean basis, the Jacobian is the change in volume.

In this section the deformation gradient is multiplicatively decomposed into expansion part \mathbf{F}^{θ} and volume preserving part $\bar{\mathbf{F}}$. This is a direct consequence of the actual deformation being written as composition of two parts. The intermediate configuration is stress free and purely fictitious. But, no attempt will be made to compute solutions or impose equilibrium in that state.

This method was first suggested for expansion in [4]. The deformation gradient is written as,

$$\boldsymbol{F} = \boldsymbol{F}^{\theta} \boldsymbol{\bar{F}} \tag{11}$$

The multiplicative split in the deformation gradient permits, in finite deformation framework, a consistent method of incorporating large expansion.

This decomposition can be substituted in any free energy function to derive the final form in which $J^{\theta} = \det[\mathbf{F}^{\theta}]$ represents the expansion. For the case at hand, the expansion is known to be 2.2.

V. NUMERICAL EXAMPLES

The formulation described above was implemented within a general purpose finite element program FEAP [8]. The element technology incorporated a staggered scheme to solve the coupled problem. Three sets of coupled equations were set up to solve for four variables per node. The variables are, two displacements, one concentration and one level set variable.

Some of the crucial achievements of this work are the following: the $Si-SiO_2$ interface does not need to coincide with element boundaries, expansion of SiO_2 is incorporated into the constitutive equations since it is a material property, a general viscoelastic model is implemented.

Incompressibility can be handled within the three field Hu–Washizu type mixed variational formulation without running into problems of "locking". The incompressibility constraint in enforced by an augmented Lagrangian formulation.

The cylinder oxidation problem (shown in Fig[2]) was performed to test the code. The interface movement, diffusion with discontinuities and the viscoelastic stress problem with expansion have been solved in a staggered format. The mechanical part is non-linear, the diffusion equation is linear and the boundary motion is explicit. The time-step stayed unchanged throughout. The timestep size was determined by the explicit scheme for the boundary motion equation. No remeshing was required and the entire problem took 600 time-steps.

VI. CONCLUSIONS

The new formulation releases the restriction of requiring the $Si-SiO_2$ interface to element edges. The expansion formulation with the level-set description obviates the need for remeshing except for error based adaptation. "Locking" phenomenon is overcome by means of an augmented Lagrangian method within mixed finite element interpolations. A general thermodynamically consistent viscoelastic model has been used. This setting can be used as a platform to test various problems involving growth and different constitutive models like oxidation and silicidation.

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Fig. 1. Enhancements to shape functions in 1-D and 2-D



Fig. 2. Initial($t = 0\Delta t$), intermediate($t = 300\Delta t$) and final states($t = 600\Delta t$).