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Implementation and application of some nonlinear models of diffusion/reaction in solids

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ABSTRACT

Feulvarch et al. [5] defined an extended class of nonlinear models of diffusion/reaction in solids, applicable to both problems of diffusion of heat with phase change, and problems of diffusion of chemical elements with formation of simple, "stoechiometric" precipitate phases. They also presented an efficient finite element implementation of this class of models, based on a two-field formulation coupled with an implicit time-integration. This paper extends this earlier work in various ways. First it is shown that the class defined encompasses more elaborate models of diffusion of chemical elements with formation of complex, "non-stoechiometric" precipitate phases, consisting of solid solutions of "stoechiometric" constituents in variable proportions. Second, a more economical finite element implementation based on a one-field formulation - thus halving the number of nodal unknowns - is proposed. The keypoint in the new algorithm lies in an improved treatment of boundary conditions. Third, applications of this new algorithm pertaining to problems of internal oxidation of steel sheets are presented. Four distinct, practically significant situations are considered: (i) the case of a single, highly oxidizable element, with a reference to the seminal analytical solution of Wagner [27]; (ii) the case of a complex system involving 5 oxidizable elements and 9 *a priori* possible oxides; (iii) the case of a single oxidizable element but with formation of a non-stoechiometric oxide; (iv) a 2D case involving preferred diffusion along grain boundaries.

1. Introduction

An extended class of nonlinear models of diffusion/reaction in solid matrices has been defined by Feulvarch et al. [5]. These authors showed that this class does not only encompass the classical equation of heat diffusion with phase change, but also less standard models of diffusion of chemical elements with formation of precipitate phases, defined in their simplest form by Wagner [27] in the case of internal oxidation of steels, and later gradually extended to more complex cases by Fortunier et al. [6], Huin et al. [13] and Brunac et al. [1]. The common feature of these models is that in the diffusion equations, the unknown quantities appearing in the left-hand side (LHS) involving a time-derivative, and the right-hand side (RHS) involving the divergence of a flux, are different, unlike in a simple heat diffusion equation. These two unknowns are however related since that in the RHS is a well-defined, given function of that in the LHS - the converse being not true, the function in question being not necessarily invertible. For instance, for heat diffusion with phase change, the unknown in the LHS is the enthalpy per unit volume and that in the RHS is the temperature: the temperature is a well-defined function of the enthalpy, but the enthalpy is not a well-defined function of the temperature in the case of phase change at a fixed temperature.

Feulvarch et al. [5] have also presented an innovative finite element algorithm for numerical solution of the boundary-value problem for this class of models. The two major features of this algorithm are: (i) a two-field formulation involving both unknowns appearing in the LHS and the RHS; and (ii) an implicit time-integration. The advantages of the new algorithm are as follows:

- In the case of heat diffusion with phase change:
  1. Since it considers the *enthalpy* (which makes it similar, if not identical, to so-called *enthalpic methods* developed by Mundim and Fortes [18], Droux [4], Gremaud [12], Pham [23], Nedjar [19], among others), it offers a natural and unified treatment of

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phase changes occurring both at some fixed, given temperature and over some finite temperature range.
2. Since it also considers the *temperature*, it permits to evaluate the thermal gradient directly from the temperature field, rather than by using the derivative of the function connecting the temperature to the enthalpy plus the enthalpy gradient. This is an advantage in the case of a phase change occurring at a fixed temperature, because the latter method is then hampered by the spatial discontinuity of the derivative of the function connecting the temperature to the enthalpy.
3. Its implicit scheme for time-integration warrants a good numerical stability.

- In the case of diffusion of chemical elements with formation of precipitate phases:
  1. Its use of finite elements makes the meshing, in the case of 2D and 3D problems, much easier than in the approach of Huin et al. [13] and Brunac et al. [1] based on finite differences.
  2. Its implicit time-integration also permits to use large time-steps without any apparent degradation of the results; this again represents an advantage over the approach of Huin et al. [13] and Brunac et al. [1] based on explicit time-integration, which required careful (but nevertheless often inefficient) control of the time-step.

The main drawback of Feulvarch et al. [5]'s two-field algorithm, however, is that the number of degrees of freedom (DOF) per node is twice that in a more customary one-field approach. This is *not* a serious shortcoming for problems of heat diffusion with phase change because the number of DOF per node is small anyway, be it 1 or 2. But it *is* a drawback for problems of diffusion of chemical elements with formation of precipitate phases, which frequently involve 5 or more elements: increasing the number of DOF per node means making the simulations longer, and more importantly the convergence of the iterative procedure at each time-step harder, if not impossible.

In order to obviate this difficulty, Feulvarch et al. [5] tentatively proposed to eliminate the nodal DOF pertaining to the RHS so as to retain only those pertaining to the LHS. But this suggestion raises an insurmountable difficulty tied to boundary conditions (BC) of Dirichlet type. It so happens that in the class of problems considered, these BC involve the unknowns in the RHS, not the LHS. For instance, in problems of heat diffusion with phase change, Dirichlet BC involve the temperature, not the enthalpy. If Dirichlet BC are treated by a standard penalty method, the elimination of the nodal DOF pertaining to the RHS leads, in the "reduced" nonlinear system on the nodal DOF pertaining to the LHS, to very large off-diagonal terms of the tangent-matrix which prevent convergence of the iterations.

The aim of this paper is to pursue the work of Feulvarch et al. [5] in several directions. Attention will essentially be focussed on elaborate models of diffusion of chemical elements with formation of precipitate phases, but the case of heat diffusion with phase change will also be considered incidentally, to provide a simple illustration of the main ideas.

We shall focus here on three features:

- First, we shall show that the class of models defined by Feulvarch et al. [5] encompasses more complex models of diffusion of chemical elements with formation of precipitate phases than considered up to now. Fortunier et al. [6], Huin et al. [13] and Brunac et al. [1] all assumed that the precipitate phases were "stoechiometric" in the sense that their chemical composition was defined unambiguously: MnO, Al_2O_3, etc. But more complex, "non-stoechiometric" phases are often encountered in the metallurgical industry, in the form of solid solutions of stoechiometric constituents with well-defined chemical composition, but in variable, *a priori* unknown proportions: for instance $(FeO)_x(MnO)_{1-x}$, with $0 \leq x \leq 1$. An extended model incorporating such phases will be defined and shown to still fit within Feulvarch et al. [5]'s theoretical framework.
- Second, an innovative one-field finite element algorithm solving the difficulties of Feulvarch et al. [5]'s two-field approach, while retaining its advantages, will be proposed. The key point in the new algorithm lies in a special treatment of Dirichlet BC permitting to eliminate the nodal DOF pertaining to the RHS. This treatment is possible only for a special subclass of Feulvarch et al. [5]'s class of models; but all examples of models considered by Feulvarch et al. [5] and in this paper fall within this subclass.
- Third, we shall present some applications of the new numerical algorithm, implemented in the SYSWELD® finite element code developed by ESI-Group. The examples chosen all pertain to problems of internal oxidation of steel sheets, of practical interest in the metallurgical industry. Most of them are 1D but may involve complex physical situations and/or raise drastic numerical difficulties, owing to severe nonlinearities. The final example involves a 2D problem. (Considering fully 3D problems would not raise any other problem than the heaviness and cost of the simulations).

The paper is organized as follows:

- Section 2 briefly presents, as a prerequisite, Feulvarch et al. [5]'s class of nonlinear models of diffusion/reaction in solids.
- Section 3 recalls, as a first, elementary but illuminating example, the heat diffusion equation with phase change and shows how its fits into Feulvarch et al. [5]'s theoretical framework.
- Section 4 presents, as a more elaborate example, a model of diffusion of chemical elements with formation of precipitate phases, extending those studied by Fortunier et al. [6], Huin et al. [13] and Brunac et al. [1] through consideration of non-stoechiometric phases. The proof of the fact that this extended model still belongs to the class defined by Feulvarch et al. [5] will require a careful mathematical investigation of the "problem of local thermodynamic equilibrium", defining the unknowns in the RHS of the diffusion equations as functions of the unknowns in the LHS.
- Section 5 presents an innovative algorithm for numerical solution of the boundary value problem by the finite element method, considering nodal DOF pertaining to the sole LHS of the diffusion equations.
- Section 6 considers, as a first application, the case of 1D, isothermal internal oxidation of a steel sheet containing a single, highly oxidizable alloying element (very low solubility product of the oxide). This problem was solved analytically almost 60 years ago by Wagner [27], whose solution quickly became a cornerstone of the science of internal oxidation. This reference solution is used to critically assess the algorithm proposed, in some "numerically tough" case.
- Section 7 considers a still 1D, but nevertheless much more complex problem of anisothermal internal oxidation, involving 5 chemical elements, 9 *a priori* possible precipitate phases, and a variable (prescribed) temperature.
- Section 8 comes back to a simpler case involving isothermal diffusion of only two elements and precipitation of a single oxide, but a non-stoechiometric one.
- Finally Section 9 considers a 2D problem of isothermal internal oxidation again involving only two diffusing elements and a single oxide, but with enhanced diffusion along grain boundaries.

2. Feulvarch et al.'s [5] class of nonlinear models of diffusion/reaction

2.1. Field equations

The models considered by Feulvarch et al. [5] involve two n-vector-valued functions of position and time, $\mathbf{u} \equiv (u_i)_{1 \leq i \leq n}$ and $\mathbf{v} \equiv (v_i)_{1 \leq i \leq n}$, satisfying the following field equations in the domain Ω considered: