Numerical simulation of superficial diffusion and precipitation of chemical elements, with application to some nitriding process

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Abstract

A new option for numerical simulation of simultaneous diffusion and precipitation of chemical elements in metallic matrices has been developed within the SYSWELD finite element programme. The simulation can include arbitrary numbers of diffusing elements and precipitate phases. Diffusion is described using Fick’s law. Precipitation is assumed to obey kinetic equations of the Johnson-Mehl type; thermodynamic equilibrium between the phases, as determined by the law of mass action, plays a fundamental role in these equations. The finite element implementation treats diffusion in the standard way, precipitation being accounted for through iterative adjustment of the “source terms” in the diffusion equations. As an example, a simulation of the diffusion of nitrogen and precipitation of chromium nitride in a gear tooth, arising from some nitriding process, is presented. It allows to evaluate the distortions arising from the volume expansion accompanying the formation of chromium nitride.

1 Introduction

The SYSWELD finite element code [1], essentially devoted to the simulation of welding processes and heat treatments of metals, has been developed by the ESI Group with various academic partners for more than 20 years, and
many applications to the study of industrial problems have been performed. Special emphasis is placed in this software on the accurate description of metallurgical phase changes and their consequences on the mechanical behaviour.

Heat treatments are often preceded by carburization or nitridation processes, which involve simultaneous diffusion and precipitation of various chemical elements. Another example of such phenomena is internal oxidation. Also, more refined descriptions of metallurgical transformations themselves would require simulating such processes and incorporating their influence upon phase changes. For all these reasons, it appears desirable to extend SYSWELD's capabilities by developing an option for simulation of simultaneous diffusion and precipitation of chemical elements. This has been done recently, and the present stage of development and capabilities of the software are presented here. No connection with the other metallurgical capabilities of SYSWELD has been developed up to now, the only possible "coupling" being to use the results of some preliminary thermal calculation in the diffusion-precipitation simulation. This already allows, however, for such interesting applications as the study of internal oxidation or nitriding processes.

The paper is organized as follows. Section 2 presents the model employed, which appears as a rather straightforward extension of Wagner's [2] classical model for internal oxidation (and its later more or less refined variants due to Rapp [3], Bongartz et al. [4], Whittle et al. [5]...) to arbitrary numbers of diffusing species and precipitate phases; the main difference is that the governing nonlinear equations are retained in their full complexity, no attempt being made to simplify them by considering special cases or introducing approximations in order to derive analytical solutions. Section 3 presents the finite element implementation of the model. The diffusion equations are treated in the standard way and precipitation by iteratively correcting the nonlinear "source terms" in these equations. Finally, Section 4 presents an application to the simulation of a nitriding process conducted by the Eurocopter company on a gear tooth. The calculation is fully 3D and involves more than 1,000,000 elements and nodes. The distortions resulting from the formation of chromium nitride are evaluated; the ultimate goal here is to optimize the process in order to minimize these distortions.

2 Theoretical model

2.1 General hypotheses

One considers, within some metallic matrix phase ($Fe$ generally), $n_x$ alloying elements ($Mn, O, Al, Ti, C$...) referred to with a Latin index $i$. The mass fraction of element $i$ dissolved in the matrix is denoted $F_i^D$, its total mass fraction (in all its forms, dissolved in the matrix or embedded in precipitates) $F_i^T$, and its molar mass, $M_i$. 
There are $n_p$ possible precipitate phases ($\text{MnO}$, $\text{Al}_2\text{O}_3$, $\text{TiC}$...) noted with a Greek index $\alpha$. The stoechiometric coefficient of element $i$ in precipitate $\alpha$ is noted $N_{i\alpha}$; that is, there are $N_{i\alpha}$ atoms of element $i$ in each molecule of precipitate $\alpha$. The mass fraction of precipitate $\alpha$ is noted $F^P_\alpha$, and its molar mass, $M_\alpha$.

Counting atoms of a given element in all the possible forms, one gets:

$$\frac{F_i^T}{M_i} = \frac{F_i^D}{M_i} + \sum_{\alpha=1}^{n_p} N_{i\alpha} \frac{F^P_\alpha}{M_\alpha}, \quad i = 1, 2...n_e. \quad (1)$$

### 2.2 Diffusion equations

The diffusion of each element in the matrix is assumed to obey Fick’s law:

$$\frac{\partial F_i^T}{\partial t} = \nabla \cdot (D_i \nabla F_i^D), \quad i = 1, 2...n_e \quad (2)$$

where $D_i$ denotes the diffusion coefficient of the element. Note that it is the total fraction of element $i$ that appears in the left-hand side, because it is the variations of the total numbers of atoms of the various species in a given volume that are governed by the fluxes of these species through the boundary of this volume. On the other hand the right-hand side involves the sole dissolved fraction of element $i$, because atoms trapped in precipitates cannot contribute to the fluxes.

### 2.3 Precipitation equations

The evolution of the fraction of precipitates is assumed to be governed by a local kinetic equation of the Johnson-Mehl type [6]:

$$\frac{\partial F^P_\alpha}{\partial t} = n_\alpha f_\alpha (F^{P_\alpha}_e - F^P_\alpha) \left( \ell n \frac{F^{P_\alpha}_e}{F^{P_\alpha}_e - F^P_\alpha} \right)^{(n_\alpha - 1)/n_\alpha}, \quad \alpha = 1, 2...n_p. \quad (3)$$

In this expression, the exponent $n_\alpha$ and the frequency $f_\alpha$ are material parameters. Also, $F^{P_\alpha}_e$ denotes the fraction of precipitate $\alpha$ corresponding to thermodynamic equilibrium (for given, fixed total fractions of all elements), the calculation of which is explained below. This heuristic evolution equation expresses the tendency of the fraction $F^P_\alpha$ of precipitate $\alpha$ to “relax” toward its equilibrium value $F^{P_\alpha}_e$.

### 2.4 Determination of thermodynamic equilibrium

Thermodynamic equilibrium, for given total fractions $F_i^T$ of all elements, is determined by the law of mass action, which stipulates that for every $\alpha = 1, 2...n_p$:

$$\text{either } F^{P_\alpha}_e > 0 \text{ and } \prod_{i=1}^{n_e} (F_i^{D_\alpha})^{N_{i\alpha}} = K_\alpha \quad (4)$$
The precipitate is present in the first case and absent in the second. In these equations, $F_i^{De}$ denotes the equilibrium dissolved fraction of element $i$, tied to the equilibrium fractions of precipitates $F_i^{Pe}$ and the total fraction of this element $F_i^T$ by an expression similar to (1), and $K_i$ is the solubility product of precipitate $\alpha$.

2.5 Boundary conditions

Boundary conditions are taken in the classical form:

$$D_i \nabla F_i^D \cdot n - J_i + \lambda_i (F_i^D - F_i^{Dext}) = 0, \quad i = 1, \ldots, n_e$$

(6)

where $n$ is the normal vector to the boundary, $J_i$ some prescribed input flux, $\lambda_i$ some transfer coefficient and $F_i^{Dext}$ some “external activity”.

3 Finite element implementation

3.1 Time discretization

A generalized Euler scheme is adopted for the total fractions of elements:

$$F_i^T - F_i^{T,0} = \Delta t \left[ (1 - \nu) \frac{\partial F_i^{T,0}}{\partial t} + \nu \frac{\partial F_i^T}{\partial t} \right], \quad i = 1, \ldots, n_e$$

(7)

where $0 < \nu \leq 1$ and the presence, or absence, of an index $0$ indicates that the quantity considered is taken at the beginning, or the end, of the time interval $[t, t + \Delta t]$ considered, respectively. Combination of equations (2) and (7) then yields:

$$\nabla.(D_i \nabla F_i^D) = \frac{F_i^T}{\nu \Delta t} - \frac{1 - \nu}{\nu} \frac{\partial F_i^{T,0}}{\partial t} - \frac{F_i^{T,0}}{\nu \Delta t}, \quad i = 1, \ldots, n_e.$$  

(8)

With regard to the kinetic equations for precipitation (3), we consider all coefficients in these equations as constant in the interval $[t, t + \Delta t]$ and then integrate them exactly, which yields:

$$F_i^P = F_i^{Pe} \left\{ 1 - \exp \left[ - (f_\alpha (t + \Delta t - t_{\alpha,0}))^{n_\alpha} \right] \right\}, \quad \alpha = 1, \ldots, n_p$$

(9)

where $t_{\alpha,0}$ is the instant determined by the condition:

$$F_{\alpha,0}^P = F_{\alpha}^{Pe} \left\{ 1 - \exp \left[ - (f_\alpha (t - t_{\alpha,0}))^{n_\alpha} \right] \right\}. \quad (10)$$

The advantage of such an exact integration is to reduce the constraints on the time step $\Delta t$ to the requirement that it be smaller than the sole characteristic time for diffusion.
3.2 Calculation of dissolved fractions of elements from total fractions - Spatial discretization

Momentarily assuming the $F_i^T$ (plus of course the $F_{i,0}^T$ and $\partial F_{i,0}^T/\partial t$) to be known, one can calculate the $F_i^D$ by applying Galerkin’s method to the diffusion equations. Thus, interpolating the $F_i^D$ using their nodal values $F_{i,q}^D$ ($q \equiv$ index of node) and the shape functions $N_q$, multiplying (8) by $N_p$, and integrating by parts using (6), one gets:

$$\int_{\Omega} \left[ -D_i \sum_q F_{i,q}^D \nabla N_p \cdot \nabla N_q + \left( -\frac{F_{i,q}^T}{\nu \Delta t} + \frac{1 - \nu}{\nu} \frac{\partial F_{i,0}^T}{\partial t} + \frac{F_{i,0}^T}{\nu \Delta t} \right) N_p \right] d\Omega$$

$$+ \int_{\partial \Omega} \left[ J_i + \lambda_i \left( F_{i,ext}^D - \sum_q F_{i,q}^D N_q \right) \right] N_p \, dS = 0 , \quad (11)$$

where $\Omega$ is the domain considered and $\partial \Omega$ its boundary. The set of such equations, for all values of $i$ and $p$, is a linear system in the unknowns $F_{i,q}$, the solution of which provides the values of these fractions.

3.3 Calculation of fractions of precipitates from total fractions of elements - Minor iterations

One can also deduce the values of the $F_i^P$ from those of the $F_i^T$, calculating first their equilibrium values $F_i^{P,e}$ and then using (9) and (10) (the $F_{i,0}^{P,e}$ being of course known). To find the state of thermodynamic equilibrium, equations (4,5) must be used.

Provided that the set of “existing” precipitates (that is such that $F_i^{P,e} > 0$) is known, (4) provides $n$ ($\leq n_p$) equations on the $n$ unknown fractions of these precipitates (the $F_i^{P,e}$ being known in terms of the $F_i^T$ and the $F_i^{P,e}$ through (1)), which can be solved by Newton’s method.

To find the set of “existing” precipitates, an iterative procedure must be used. For a given set, at a given iteration, solving equations (4) yields the values of the corresponding $F_i^{P,e}$. A posteriori verifications are then necessary. If some precipitate which was assumed to exist is found to have a negative $F_i^{P,e}$, it must be eliminated from the next set of “existing” precipitates, in the next iteration. If a precipitate which was assumed not to exist ($F_i^{P,e} = 0$) is found to have a ratio $\prod_{i=1}^{n} F_i^{P,e}/N_i > K_i$ larger than unity (violation of (5)), it must be added to this set. The process must be repeated until a posteriori verifications result in no change in the set of “existing” precipitates.

Thus determination of the state of thermodynamic equilibrium involves 2 interwoven sets of “minor” iterations (in contrast to the “major” iterations explained below): iterations on the assumed set of “existing” precipitates, and within each of these iterations, Newton iterations aimed at solving equations (4).
In contrast to the calculation of the $F^D_i$ from the $F^T_i$, which implies solving a linear system involving all nodes of the structure, that of the $F^P$ is a purely local operation, all points being treated independently. In practice, it is performed at all Gauss points of the structure.

3.4 Calculation of total fractions of elements - Major iterations

We have thus seen how to determine both the $F^D_i$ and $F^P_\alpha$ from the $F^T_i$; but the $F^T_i$ are in fact unknown. To calculate them, one may perform "major" iterations as follows: starting from some initial trial values for the $F^T_i$, for instance $F^T_{i,0} + (\partial F^T_i/\partial t) \Delta t$, calculate the $F^D_i$ and $F^P_\alpha$ as sketched above, then use (1) to get some new values of the $F^T_i$, and repeat the process until convergence is reached. Of course, each such "major" iteration involves "minor" iterations of the type explained above.

In practice, since the $F^P_\alpha$ are calculated at the Gauss points, the $F^T_i$ are also calculated there (using the values of the $F^D_i$ at the Gauss points deduced from their nodal values). The choice of Gauss points for calculation of the $F^P_\alpha$ and $F^T_i$ is compatible with the necessary evaluation of integrals involving the $F^T_i$ (see (11)).

Once the $F^T_i$ are known, the $\partial F^T_i/\partial t$ may be deduced from (7). Also, the $F^P_\alpha$ have been calculated in the process of evaluating the $F^T_i$. Hence all relevant quantities are known for the next time step.

4 Application: simulation of some nitriding process

4.1 Presentation of the problem

We shall now present, as an illustrative example, some simulation of a nitriding process performed on a gear tooth by the Eurocopter company. Nitriding results in the formation of a chromium nitride precipitate phase. Its aim is to improve the superficial mechanical properties of the material. Unfortunately, precipitation of chromium nitride is accompanied by a change of specific volume, and this generates undesired distortions of the gear which must be anticipated, and this can be done only numerically.

4.2 Geometry and mesh

A typical portion of the gear is shown on Figure 1. For symmetry reasons, only half a tooth need be modelled. Figure 2 shows the mesh of such a half-tooth. Because it is 3D and quite refined near the surface (nitridation occurring only in the first millimeter), there are as many as 1,110,000 elements and 1,130,000 nodes.
Figure 1: Geometry of the gear.

Figure 2: Mesh of the zone modelled.
4.3 Simulation of diffusion and precipitation

The simulation involves diffusion of nitrogen and chromium (but that of chromium is almost negligible), and precipitation of chromium nitride. It disregards, in this first, simple approach, diffusion of carbon, intragranular substitution of carbon atoms by nitrogen atoms near the surface, and intergranular precipitation of chromium carbides deeper under this surface.

Figures 3, 4 and 5 show the final mass percentages of dissolved nitrogen, dissolved chromium and chromium nitride precipitate, in a typical vertical section of the mesh shown in Figure 2.

Figure 3: Final mass percentage of dissolved nitrogen.

Figure 4: Final mass percentage of dissolved chromium.

Figure 5: Final mass percentage of chromium nitride.
4.4 Mechanical simulation

The specific volume of chromium nitride being slightly larger than that of the ferritic matrix, its precipitation generates residual stresses and distortions. A mechanical calculation, using the results of the preceding diffusion-precipitation simulation as input data and assuming elastic behaviour, has been performed to evaluate these distortions and stresses. Figure 6 shows the deformed mesh with superimposed zones of equal von Mises stresses. The displacements here are amplified by a factor of 100 in order for the distortions to be visible. The von Mises stress does not exceed the yield limit of the material, except in small regions; this essentially validates the hypothesis made of purely elastic behaviour.

![Figure 6: Deformed mesh and zones of equal von Mises stresses.](image)

4.5 Closure

Both the distortions and the stresses resulting from the simulation seem to be reasonable. In particular, superficial compression stresses are found, as expected.

One can now study the effect of various parameters such as chemical composition, geometry of the gear and parameters of the nitriding process.
Diffusion of carbon, intragranular substitution of carbon atoms by nitrogen atoms near the surface and deeper intergranular precipitation of chromium carbides will also be included in a future study. Simulation of elimination of a superficial layer (aimed at reducing distortions), and of subsequent fatigue of the gear during service can also be envisaged.

One can therefore envisage to improve service performances through purely numerical parameter studies, thus reducing experimental costs.

References