pcpsim
MODEL FOR HOMOGENEOUS PRECIPITATION KINETICS in GNU OCTAVE

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1 Introduction

The model for homogeneous isothermal precipitation is partly based on the model by Langer and Schwartz, as modified by Kampmann and Wagner (MLS model) and describes the nucleation and growth of precipitates from a solid solution.

2 Classical Theory of Nucleation and Growth

As a first step we need to define the driving force for precipitation at any given time of the aging process:

$$\Delta g = -\frac{kT}{V_{at}} \cdot S \tag{1}$$

with

$$S = X_p \ln \frac{X}{X_{eq}} + (1 - X_p) \ln \frac{1 - X}{1 - X_{eq}} \tag{2}$$

where V_{at} is the atomic volume (considered as constant for all species, $V_{at} = a^3/2$ for a bcc structure with lattice parameter a), S is a thermodynamical function giving the driving force for nucleation (based on the hypothesis of a diluted and regular solid solution), X_{eq} is the equilibrium solute mole fraction in the matrix, X_p the solute mole fraction in the precipitate, and X the current solute mole fraction of the matrix.

The nucleation rate is:

$$J_s = \frac{dN}{dt} = Z\beta^* \exp(-\frac{\Delta G^*}{kT}) \exp(-\frac{t_i}{t}) \tag{3}$$

where N is the number of nuclei per atomic site, Z is the Zeldovich factor ($\approx 1/20$) and t_i is the incubation time. The other parameters of equation are expressed as follows:

$$\beta^* = \frac{4\pi R^{*2} D X}{a^4} \tag{4a}$$

$$R^* = \frac{2\gamma V_{at}}{S\,kT} \tag{4b}$$

$$\Delta G^* = \frac{4}{3}\pi R^{*2}\gamma \tag{4c}$$

$$t_i = \frac{1}{2\beta^* Z} \tag{4d}$$

where R^* and ΔG^* are the critical nucleation radius and free energy, respectively, γ is the matrix/precipitate interfacial energy and D is the diffusion coefficient of solute atoms in the matrix.

The precipitate size increase during a time increment dt is then calculated as:

$$\frac{dR}{dt} = \frac{D}{R} \cdot \frac{X - X_R}{X_p - X_R} + \frac{1}{N}\frac{dN}{dt} \cdot (\alpha R^* - R) \tag{5}$$

The first term on the left hand side of (5) corresponds to the growth of existing precipitates (including the Gibbs-Thomson effect). X_R represent the matrix solute concentration at the interface ($r = R$) as modified by surface tension according to the Gibbs-Thomson effect. For an ideal solution X_R is given by (Wagner et al., 2005; Calderon et al., 1994):

$$X_R = X_{eq} \cdot \exp\left(\frac{2\gamma V_{at}}{kT\,R}\frac{1 - X_{eq}}{X_p - X_{eq}}\right) \tag{6}$$

The second term of (5) is due to the appearance of new nuclei of size αR^*. The numerical factor $\alpha = 1.05$ results from the fact that new precipitates only grow if their size is slightly larger than the nucleation size.

Finally, the coupling between the precipitation density and their mean radius is made through the solute balance:

$$X_0 = X\,(1 - F) + X_p\,F \tag{7}$$

where $F = \frac{4}{3}\pi R^3 N$ is the precipitate volume fraction.

2.1 Dimensionless formulation

Now the following dimensionless variables are defined that are easier to use for programming:

$$t' = \frac{D \cdot t}{r_{at}^2} \tag{8a}$$

$$R' = R/r_{at} \tag{8b}$$

The equations (3), (5) plus the differential of the solute balance constitute a system of differential equation for N, R' and X, which is rewritten here in terms of dimensionless variables:

$$\frac{dN}{dt'} = \frac{\beta_0 X}{S^2} \exp\left(-\frac{\Delta G_0}{S^2}\right) \exp\left(-\frac{S^2}{2\beta_0 X t'}\right) \tag{9a}$$

$$\frac{dR'}{dt'} = \frac{X - X_R}{X_p - X_R}\,\frac{1}{R'} + \frac{1}{N}\frac{dN}{dt'}\left(\frac{\alpha R_0}{S} - R'\right) \tag{9b}$$

$$\frac{dX}{dt'} = -(X_p - X)\,\frac{F}{1-F}\left[3\frac{\dot{R}'}{R'} + \frac{\dot{N}}{N}\right] \tag{9c}$$

where the following definitions have been made

$$R_0 = \frac{2\gamma V_{at}}{r_{at} kT} \tag{10a}$$

$$\beta_0 = 4\pi R_0^2 Z r_{at}^4 / a^4 \tag{10b}$$

$$\Delta G_0 = \frac{4\pi R_0^2 r_{at}^2 \gamma}{3kT} \tag{10c}$$

$$X_R = X_{eq} \exp\left(\frac{R_0}{R}\frac{1 - X_{eq}}{X_p - X_{eq}}\right) \tag{10d}$$

$$F = R'^3 N \tag{10e}$$

In the following we will omit the prime from t' and R'.

3 Numerical evolution of the precipitate distribution function (PDF)

In this type of modelling, first discussed by Kampmann & Wagner (see Wagner et al. (2005), the “N-modell”,) we consider the evolution of the precipitate distribution function with respect to radius, $f(R,t)$. The distribution satisfies the equation of continuity:

$$\frac{\partial f}{\partial t} + \frac{\partial}{\partial R}(f \cdot v_R) = J_s \cdot \delta(R - \alpha R^*) \tag{11}$$

where the precipitate growth rate $v_R = dR/dt$ is given by the 1st term on the right side of (5). The source term on the right side of (11) describes the generation of new nuclei with radius αR^* at a rate given by J_s from eq. (3).

This PDE is solved numerically by discretizing the (t, R) space and approximating the partial derivatives by finite differences. Defining the grid points (t_i, R_k), where (i, k) are integers, the discretized distribution is defined as

$$f_{ik} = \frac{1}{\Delta R_k} \int_{R_{k-1}}^{R_k} f(R, t_i)\, dR \tag{12}$$

and the discretized PDE becomes

$$\frac{f_{i+1,k} - f_{ik}}{\Delta t_i} + \frac{J_{ik} - J_{i,k-1}}{\Delta R_k} = \frac{J_s}{\Delta R_{k^*}} \delta_{k,k*} \tag{13}$$

where the precipitate "current" J_{ik} is given by

$$J_{ik} = \begin{cases} f_{ik} v_k & v_k > 0 \\ -f_{i,k+1} v_k & v_k < 0 \end{cases} \tag{14}$$

The index k^* corresponds to the spatial grid point where $R_{k^*} \leq \alpha R^* < R_{k^*+1}$.

The above finite difference scheme is taken from Myhr and Grong (2000) and corresponds to "*upwind differencing*" used in CFD (see Press et al. "Numerical Recipes", ch. 20).

The total precipitate concentration, average radius and volume fraction can be obtained from the distribution by the following relations:

$$N_i = \sum_k f_{i,k} \Delta R_k \tag{15a}$$

$$\bar{R}_i = (1/N_i) \sum_k f_{i,k} R_k \Delta R_k \tag{15b}$$

$$F_i = (1/4) \sum_k f_{i,k} (R_k^4 - R_{k-1}^4) \tag{15c}$$

3.1 Numerical integration

A static logarithmic grid is selected for the R-space discretization. $\Delta R_k / R_k$ is constant (typically ~ 0.05.) The first point is positioned at or just below R^* and the last point should be higher than the largest expected R.

From (13) it is evident that $f_{i+1,k}$ can be calculated from f_{ik} after deciding the time step Δt_i. This is selected so that

$$v_k \Delta t_i < \Delta R_k / 2, \quad \forall k \tag{16}$$

This is the well-known *Courant condition* which ensures the stability of the numerical solution (again see Press et al. "Numerical Recipes", ch. 20). Essentially it means that in one time-step nuclei from one distribution bin can move only to adjacent bins and not further away. To satisfy the above condition the time interval is set by

$$\Delta t_i = 0.5 \min \{|\Delta R_k / v_k|\} \tag{17}$$

If the simulation extends beyond the nucleation stage and the average R has evolved well above $R*$, the nuclei concentration close to R^* becomes very low and thus the first few bins of the distribution can be neglected. Thus we define a lower cut-off index k_c and set $f = 0$ for $R < R_{k_c}$. The grid points below k_c are then not considered when selecting Δt_i. This speeds-up significantly the integration in the growth phase. As can be seen from the last equation, for a logarithmic grid we have $\Delta R_k / v_k \sim 0.05 R_k / v_k$ which becomes very small as $R_k \to R^*$. Neglecting the grid points near to R^* allows for much larger Δt values in the growth regime.

The cut-off index k_c is initially set to the 1st grid point and then it is advanced by one each time the concentration in the 1st bin above cut-off, $f_{i,k_c+1} \cdot \Delta R_{k_c+1}$, falls below a certain threshold N_{min}. A reasonable threshold could be 1 nucleus per cm^3 or, equivalently, $N_{min} \sim 10^{-23}$. This means that effectively when the concentration in the first bin above k_c falls below N_{min}, it is zeroed-out and becomes inactive.

To account also for nuclei dissolution, where the distribution will move gradually towards smaller R, we have to allow k_c to go down again, i.e., to reactivate gradually the lower bins of the distribution. For this we check the concentration δN_c of nuclei that would move from bin $k_c + 1$ towards k_c during a time-step. This is equal to

$$\delta N_c = v_{k_c} f_{i,k_c+1} \Delta t_i$$

If δN_c becomes larger than a threshold then the cut-off index k_c is decreased by one. This threshold is selected as

$$\delta N_c \geq N_{min} + \epsilon N \tag{18}$$

where $N = \sum_k f_{i,k} \Delta R_k$ is the total concentration of nuclei and ϵ a small number (typically 10^{-3}).

References

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