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 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

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

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_C the current solute mole fraction of the matrix.

1

The nucleation rate as the time derivative of the precipitate volume density N is:

$$\frac{dN}{dt} = N_0 Z \beta^* \exp(-\frac{\Delta G^*}{kT}) \exp(-\frac{t_i}{t}) \tag{3}$$

where N_0 is the number of nucleation sites per unit volume (for homogeneous nucleation $N_0 = 1/V_{at}$), Z is the Zeldovich factor ($\approx 1/20$), t_i is the incubation time. The other parameters of equation are expressed as follows:

$$\beta^* = \frac{4\pi R^{*2} D X_0}{a^4} \tag{4a}$$

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

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

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

where R^* is the critical nucleation radius, R_0 is a thermodynamical parameter which has the dimension of a length, γ is the matrix/precipitate interfacial energy, D is the diffusion coefficient of solute atoms in the matrix, X_0 is the initial solute mole fraction.

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

$$\frac{dR}{dt} = \frac{D}{R} \cdot \frac{X_C - \hat{X}_{eq}}{\hat{X}_p - \hat{X}_{eq}} + \frac{1}{N}\frac{dN}{dt} \cdot (\alpha R^* - R) \tag{5}$$

The first term on the left hand side of (5) corresponds to the growth of existing precipitates (including the Gibbs-Thomson effect). $\hat{X}_{eq,p}$ represent the solute concentration at the interface ($r = R$) in the precipitate and the matrix, respectively, as modified by surface tension according to the Gibbs-Thomson effect. For an ideal solution they are given by (Wagner et al., 2005; Calderon et al., 1994):

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

The second term of (5) is due to the appearance of new nuclei of size R^*. 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:

$$X_0 = X_C (1 - \Phi) + X_p \Phi \tag{7}$$

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

2.1 Dimensionless formulation

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

$$\tau = \frac{D \cdot t}{a^2} \tag{8a}$$

$$\nu = N/N_0 \tag{8b}$$

$$R_0 = \frac{2\gamma V_{at}}{kT} \tag{8c}$$

$$\rho = R/R_0 \tag{8d}$$

Thus the equations (3), (5) are replaced by the following dimensionless differential equations:

$$\frac{d\nu}{d\tau} = \frac{\beta_0}{S^2} \exp\left(-\frac{\Delta G_0}{S^2}\right) \exp\left(-\frac{S^2}{2\beta_0\tau}\right) \tag{9}$$

$$\frac{d\rho}{d\tau} = \frac{a^2}{R_0^2} \frac{X_C - \hat{X}_{eq}}{\hat{X}_p - \hat{X}_{eq}} \frac{1}{\rho} + \frac{1}{\nu}\frac{d\nu}{d\tau}\left(\frac{\alpha R_0}{S} - \rho\right) \tag{10}$$

where

$$\beta_0 = 4\pi R_0^2 X_0 Z/a^2 \tag{11}$$

$$\Delta G_0 = \frac{4\pi R_0^2 \gamma}{3kT} \tag{12}$$

$$\hat{X}_{eq,p} = X_{eq,p} \exp\left(\frac{1}{\rho}\frac{1 - X_{eq,p}}{X_p - X_{eq}}\right) \tag{13}$$

Differentiating the solute balance equation we obtain the change rate of X_C:

$$\frac{dX_C}{d\tau} = -(X_p - X_C)\frac{\Phi}{1-\Phi}\left[3\frac{\dot{\rho}}{\rho} + \frac{\dot{\nu}}{\nu}\right] \tag{14}$$

where $\Phi = \Phi_0 \rho^3 \nu$, $\Phi_0 = \frac{4}{3}\pi R_0^3 N_0$.

3 Coarsening

In late stages of precipitation the nucleation rate progressively decreases because the current solute concentration in the matrix (X_C) decreases and $X_C - X_{eq} \approx 0$, this means that it is no longer supersaturated.

The precipitates continue to grow according to eq. (5). In the long time limit the LSW theory predicts that the volume of the precipitates grows linearly with time, $R^3 \propto t$.

The growth rate of R for an ideal solution in the long time limit becomes (Calderon et al., 1994)

$$\frac{dR}{dt} = \frac{4}{27} \frac{X_{eq}(1 - X_{eq})}{(X_p - X_{eq})^2} \frac{DR_0}{R^2} \tag{15}$$

Furthermore, R becomes equal to $R^* = R_0/S$ (Deschamps and Brechet, 1998) (???). In this limit the value of S is

$$S_\infty \approx (X_C - X_{eq}) \frac{X_p - X_{eq}}{X_{eq}(1 - X_{eq})} \tag{16}$$

and thus

$$X_C - X_{eq} = \frac{X_{eq}(1 - X_{eq})}{X_p - X_{eq}} \frac{R_0}{R} \propto t^{-1/3} \tag{17}$$

The precipitate volume fraction tends to the constant limiting value

$$\Phi = \frac{X_0 - X_C}{X_p - X_C} \approx \frac{X_0 - X_{eq}}{X_p - X_{eq}} = \Phi_\infty \tag{18}$$

and

$$N = \frac{3\Phi_\infty}{4\pi R^3} \propto t^{-1} \tag{19}$$

3.1 Growth and coarsening

In late stages of precipitation the nucleation rate progressively decreases because the current solute concentration in the matrix (X_C) decreases and $X_C - X_{eq} \approx 0$, this means that it is no longer supersaturated. The alloy experiences a combination of growth and coarsening. When the mean radius of precipitates (R) is much larger than the critical radius (R^*) takes places the growth phase which is described by the equations:

$$\frac{d\rho}{d\tau} = \frac{a^2}{R_0^2\rho} \frac{X_C - X_{eq}\exp(1/(X_p\rho))}{X_p - X_{eq}exp(1/(X_p\rho))} \tag{20a}$$

$$\frac{d\nu}{d\tau} = 0 \tag{20b}$$

When the mean radius and the critical radius are equal the equations follow the LSW law :

$$\frac{d\rho}{d\tau} = \frac{4}{27} \frac{X_{eq}}{1\,(or\ X_p) - X_{eq}} \frac{a^2}{R_0^2\rho} \tag{21a}$$

$$\frac{d\nu}{d\tau} = 0 \tag{21b}$$

4

Differentiating the second equation, one can deduce the variation of the matrix solute concentration with time in pure coarsening:

$$\frac{dS}{d\tau} = \frac{\dot{X}_C(X_p - X_C)}{X_C(1 - X_C)} \tag{22a}$$

$$\frac{dX_C}{d\tau} = \frac{X_C(1 - X_C)}{X_C - X_P}\frac{1}{\rho^2}\frac{d\rho}{d\tau} \tag{22b}$$

The rate of variation of the density of precipitates in pure coarsening is:

$$\frac{d\nu}{d\tau} = \frac{\dot{\rho}}{\rho}\left[\frac{X_C - (1 - X_C)}{(X_C - X_p)^2\rho}\left(\frac{1}{h\rho^3} - \nu\right) - 3\nu\right] \tag{23}$$

In order to go continuously from the growth stage to the coarsening stage, we deⓇne a coarsening fraction:

$$\frac{d\rho}{\tau} = (1 - f_{coars})\frac{d\rho}{d\tau}\ {}_{growth} + f_{coars}\frac{d\rho}{d\tau}\ {}_{coars}\frac{d\nu}{\tau} = f_{coars}\frac{d\nu}{d\tau}\ {}_{growth} \tag{24a}$$

The $f_{coars} = 0$ when $R >> R^*$ and $f_{coars} = 1$ when $R = R^*$. The f_{coars} function has the following expression which fulfills these requirements:

$$f_{coars} = 1 - erf\left(4(\rho \cdot S - 1)\right) \tag{25}$$

References

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