

# 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, modified by Kampmann and Wagner (MLS model). In this model, we treated the nucleation and growth of the precipitation.

## 2 Thermodynamics of the model

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

$$\Delta g = -\frac{kT}{V_{at}} \cdot S \quad (1)$$

with

$$S = X_p \ln\left(\frac{X_C}{X_{eq}}\right) - (1 - X_p) \ln\left(\frac{1 - X_C}{X_{eq}}\right) \quad (2)$$

where  $V_{at}$  is the atomic volume (considered as constant for all species),  $S$  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 carbon mole fraction in the precipitate, and  $X_C$  the current solute mole fraction of the matrix.

The nucleation rate as the derivative of the precipitation density  $N$  is:

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

where  $N_0$  is the number of nucleation sites per unit volume ( $\approx l/vat = 2/a^3$  for a bcc structure with lattice parameter  $a$ ),  $Z$  is the Zeldovich factor ( $\approx 1/20$ ),  $t_i$  is the incubation time. The other parameters of equation are expressed as follows:

$$\beta^* = \frac{4\pi R^{*2} D X_{C0}}{a^4} \quad (4a)$$

$$R^* = \frac{R_0}{S} \quad (4b)$$

$$R_0 = \frac{2\gamma V_{at}}{kT} \quad (4c)$$

$$\Delta G^* = \frac{16}{3} \pi \frac{\gamma}{\delta g} \quad (4d)$$

$$t_i = \frac{1}{2\beta^* Z} \quad (4e)$$

$$(4f)$$

where  $R^*$  is the nucleation critical radius,  $R_0$  is a thermodynamical parameter which has the dimension of a length,  $\gamma$  is the matrix/precipitate interfacial energy,  $D$  is the diffusion coefficient of solute atoms in the matrix,  $X_{C0}$  is the initial solute mole fraction.

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

$$\frac{dR}{dt} = \frac{D}{R} \cdot \frac{X_C - X_{eq} \exp(R_0/(X_p R))}{X_p - X_{eq} \exp(R_0/(X_p R))} + \frac{1}{N} \frac{dN}{dt} \cdot (\alpha R^* - R) \quad (5)$$

The first term corresponds to the growth of existing precipitates (including the Gibbs-Thomson effect) and the second term to the appearance of the 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:

$$X_c = \frac{X_{C0} - (4/3)\pi(X_p N R^3)}{1 - (4/3)\pi(N R^3)} \quad (6)$$

## 2.1 Nucleation and growth

Now the new dimensionless variables are defined that are easier to use for programming.

$$\tau = \frac{D \cdot t}{a^2} \quad (7a)$$

$$\nu = \frac{N}{N_0} \quad (7b)$$

$$\rho = \frac{R}{R_0} \quad (7c)$$

$$(7d)$$

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

$$\frac{d\nu}{d\tau} = \frac{\beta_0}{S^2} \exp(-\frac{\Delta G_0}{S^2}) \exp(-\frac{S^2}{2\beta_0\tau}) \quad (8)$$

$$\frac{d\rho}{d\tau} = \frac{a^2}{R_0^2\rho} \frac{X_C - X_{eq} \exp(1/(X_p\rho))}{X_p - X_{eq} \exp(1/(X_p\rho))} + \frac{1}{\nu} \frac{d\nu}{d\tau} (\frac{\alpha}{S} - \rho) \quad (9)$$

The other parameters of equation are expressed as follows:

$$\beta_0 = \frac{4\pi R_0^2 X_{C0} Z}{a^2} \quad (10a)$$

$$\Delta G_0 = \frac{(4/3)\pi R_0^2 \gamma}{kT} \quad (10b)$$

The solute balance change during a time increment dt is then calculated as:

$$\frac{dX_C}{d\tau} = h(X_C - X_p) \frac{(\dot{\nu}\rho^3 + 3\nu\rho^2\dot{\rho})}{(1 - h\nu\rho^3)} \quad (11a)$$

$$\frac{dX_C}{d\tau} = h(X_{C0} - X_p) \frac{(\dot{\nu}\rho^3 + 3\nu\rho^2\dot{\rho})}{(1 - h\nu\rho^3)^2} \quad (11b)$$

with  $h = (4/3)\pi N_0 R_0^3$

## 2.2 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:

$$\frac{d\rho}{d\tau} = \frac{a^2}{R_0^2 \rho} \frac{X_C - X_{eq} \exp(1/(X_p \rho))}{X_p - X_{eq} \exp(1/(X_p \rho))} \quad (12a)$$

$$\frac{d\nu}{d\tau} = 0 \quad (12b)$$

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

$$\frac{d\rho}{d\tau} = \frac{4}{27} \frac{X_{eq}}{1 - X_p - X_{eq}} \frac{a^2}{R_0^2 \rho} \quad (13a)$$

$$\frac{d\nu}{d\tau} = 0 \quad (13b)$$

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

$$\frac{dS}{d\tau} = \frac{X_C(X_p - X_C)}{X_C(1 - X_C)} \quad (14a)$$

$$\frac{dX_C}{d\tau} = \frac{X_C(1 - X_C)}{X_C - X_P} \frac{1}{\rho^2} \frac{d\rho}{d\tau} \quad (14b)$$

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

$$\frac{d\nu}{d\tau} = \frac{\dot{\rho}}{\rho} \left[ \frac{X_C - (1 - X_C)}{(X_C - X_p)^2 \rho} \left( \frac{1}{h\rho^3} - \nu \right) - 3\nu \right] \quad (15)$$

In order to go continuously from the growth stage to the coarsening stage, we define a coarsening fraction:

$$\frac{d\rho}{d\tau} = (1 - f_{coars}) \frac{d\rho}{d\tau}_{growth} + f_{coars} \frac{d\rho}{d\tau}_{coars} \quad \frac{d\nu}{d\tau} = f_{coars} \frac{d\nu}{d\tau}_{growth} \quad (16a)$$

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

$$f_{coars} = 1 - \operatorname{erf}(4(\rho \cdot S - 1)) \quad (17)$$