

Time-Dependent Competition Effects in Diffusion-Limited Crystal Growth

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1. Introduction

Exact analytical solution for the kinetics of a given diffusion-limited phase transformation, particularly primary crystallization of amorphous alloys, is possible to obtain at low number concentration of crystals (precipitates) using a single particle model. However, fairly often the observed nanocrystal densities are quite high and can range from 10^{21} to 10^{23} m^{-3} (e. g., in amorphous Al-based alloys) and even higher. It is clear that the local concentration of the majority phase around each precipitate is affected by the presence of neighboring precipitates. This effect is called competition or diffusive interaction. It is well known that in general the treatment of the competition effects encounter serious theoretical difficulties even for the steady state regime of growth. So up to now Ham's kinetic model of a uniformly spaced array of identical growing particles is used.

The objective of this paper is to develop an analytical approach for the description of the diffusion-limited crystal growth during primary crystallization. We generalized the notorious single precipitate model developed by Aaron et al. to the case of N growing crystals of different radii, arbitrarily located in three dimensional space and interacting due to the concentration field of the majority phase.

2. General analytical approach and some results

For growth (or dissolution) we treat the diffusion-limited transformation of spherical N precipitates in an infinite matrix by the time-dependent diffusion equation:

$$\partial c / \partial t = D \nabla^2 c \text{ in } \mathbb{R}^3 \setminus \overline{\Omega} \quad (1)$$

with the following initial and boundary conditions

$$c|_{t=0} = c_M, \quad c|_{\partial\Omega_i} = c_I, \quad c|_{r_i \rightarrow \infty} \rightarrow c_M \quad (i = \overline{1, N}); \quad (2)$$

where $c(\mathbf{r}, t)$ is the concentration field in the matrix surrounding the precipitates, whereas c_I and c_M are values of c at and far from the crystal interface; D is the volume diffusion coefficients in matrix; $\overline{\Omega} = \bigcup_{i=1}^N \overline{\Omega}_i$, where $\overline{\Omega}_i$ is the spherical region occupied by i -th crystal.

In Laplace's transform space we found the exact solution to the initial boundary-value problem (1), (2) and derived relevant Sherwood numbers which particularly for two precipitates take the form

$$\text{Sh}_i^*(s) = \frac{\pi}{2} e^{-\sqrt{\sigma_i}} \left(1 + \frac{1}{\sigma_i} \right) A_0^i + \left(\cosh \sqrt{\sigma_i} - \frac{\sinh \sqrt{\sigma_i}}{\sqrt{\sigma_i}} \right) \sum_{l=0}^{\infty} A_l^j U_{l0}, \quad i, j (\neq i) = 1, 2; \quad (2)$$

where $\sigma_i = sR_i^2/D$, $U_{lm} = (2m+1) \sum_{q=0}^{\min\{l,m\}} W_{lm}^q \sqrt{\frac{\pi \varepsilon_i}{2\sigma_i}} K_{l+m-2q+1/2} \left(\frac{\sigma_i}{\varepsilon_i} \right)$ is the diffusive interaction matrix, $\varepsilon_i = R_i/L$, L is the distance between precipitates,

$$W_{lm}^q = \frac{\Gamma(l-q+1/2)\Gamma(m-q+1/2)\Gamma(q+1/2)(l+m-q)!(l+m-2q+1/2)}{\pi\Gamma(l+m-q+3/2)(l-q)!(m-q)!}$$

and A_0^i are coefficients determined by the infinite set of linear algebraic equations

$$A_m^i + F_m^i \sum_{l=0}^{\infty} A_l^i U_{lm} = B_m^i, \quad (3)$$

where $F_m^i = I_{m+1/2}(\sigma_i)/K_{m+1/2}(\sigma_i)$, $B_m^i = \frac{2}{\pi} \left(1 - \frac{c_f}{c_M} \right) \frac{e^{\sqrt{\sigma_i}}}{\sqrt{\sigma_i}} \delta_{0m}$, $\sqrt{\pi/2z} I_{m+1/2}(z)$ and

$\sqrt{\pi/2z} K_{m+1/2}(z)$ are modified spherical Bessel functions, δ_{lm} is Kronecker delta.

Particularly in the case of two equal precipitates ($R_1 = R_2 = R$) the dependence of the characteristic relaxation time for the Sherwood number on the crystal surface $t_r^* = t_r/t_D$ (where $t_D = R^2/D$ is the characteristic relaxation time for one isolated precipitate) as a function of the relative distance $\varepsilon = R/L$ is given in Fig. 1.

We showed also that, e.g., the simple monopole approximation (4) describes well the time-dependent Sherwood number of crystals for $\varepsilon \ll 1$:

$$\text{Sh}_{\text{mon}}^*(s) = (1 + \sqrt{\sigma}) / [1 + \varepsilon \exp(-\sigma\varepsilon^{-1})]. \quad (4)$$

3. Conclusion

We presented an analytical approach for description of the diffusion-limited crystal growth during primary crystallization. For the case of two equal crystals the characteristic relaxation time and simple approximations for the time-dependent Sherwood number were obtained explicitly and analyzed. It is worth noting that our results may be applied to describe Ostwald ripening as well.

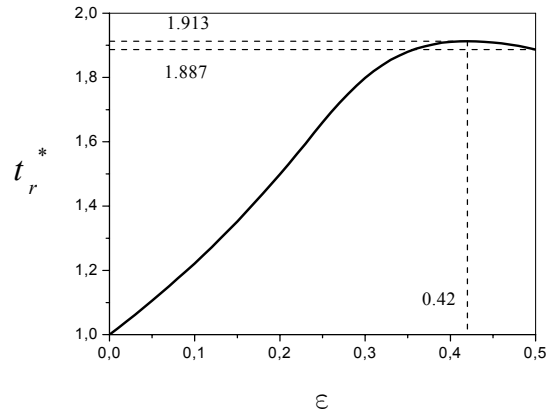


Fig. 1. Relaxation time for the time-dependent Sherwood number of the crystal.