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A model for evolution of shape changing precipitates in multicomponent systems

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Abstract

Recently the authors introduced a concept of shape factors to extend an already established model for the growth and coarsening kinetics of spherical precipitates in multicomponent multiphase environments to needle- and disc-shaped geometries. The geometry of the precipitates is kept in the original version of the concept to be self-similar with a given fixed aspect ratio. In the present treatment, the aspect ratios of individual precipitates are treated as independent evolving parameters. The evolution equations of each precipitate, described by its effective radius, mean chemical composition and the aspect ratio, are derived by application of the thermodynamic extremal principle. The driving force for the evolution of the aspect ratio of the precipitate stems from the anisotropic misfit strain of the precipitate and from the orientation dependence of the interface energy. The model is used for the simulation of the precipitation of Ti_3AlN and Ti_2AlN in Ti–Al–0.5 at.% N matrix.

Keywords: Multicomponent diffusion; Phase transformation kinetics; Precipitation; Titanium aluminides; Aspect ratio

1. Introduction and motivation

In a series of papers a new approach to modelling of precipitation kinetics in multicomponent systems has been developed [1] and applied with success to several practical cases [2,3]. The model is based originally on spherical precipitates. The concept of "shape factors" outlined in Ref. [4] has allowed investigating cylindrical precipitates with the height H_k and the diameter D_k of the precipitate k with the shape parameter (aspect ratio) $h_k = H_k/D_k$. The corresponding equivalent radius of a sphere, $\rho_k = D_k/\beta_k$ with $\beta_k = (16/(3h_k))^{1/3}$, follows from the same volume of the cylinder and of the sphere. The aspect ratio h_k, however, has been kept as a constant quantity during the evolution process. In reality the preferred shape and habit of a precipitate are determined by the requirement that the sum of the elastic strain energy and the surface energy is minimized for a given volume of a precipitate; see, e.g., Khachaturyan et al. [5]. This means that the surface energy dominates for precipitates in the nano-scale after nucleation, since the surface energy scales with the surface area compared to the volume relevant for the strain energy. As a consequence spherical precipitates, minimizing the surface energy, nucleate and grow. With the increasing size the elastic strain energy, which is a function of the misfit strain and the elastic behaviour, becomes relevant. If the misfit strain and/or the elastic behavior are anisotropic, the shape of the precipitate deviates more and more from the original spherical shape. Specially, the case of elastic anisotropy was investigated in detail by Vorhees et al., see, e.g., Ref. [6]. Of course,

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also the dependence of the interface energy on the crystallographic orientation (or, in other words, the anisotropy of the interface energy) alone would control the development of the particle shape, see, e.g., the according references in Ref. [6]. The application of the phase-field approach to find the shapes of precipitates is presented by Hu et al. [7], where a set of order parameters is introduced in addition to the concentration field and implied into the Gibbs energy. The anisotropy of the chemical energy of interfaces was studied in detail by Müller [8] for Zn-precipitates in an Al-rich Al–Zn solid.

The main goal of this paper is the development of the kinetic model for the evolution of precipitates with variable aspect ratio. The aspect ratio evolution may stem from anisotropic misfit strain together with different elastic properties of the matrix and the precipitate and the anisotropy of the interface energy. The according energetic contribution to the total Gibbs energy is added to the chemical part of the Gibbs energy. Dissipation in the system is assumed due to interface migration and diffusion. The thermodynamic extremal principle [9] allows finding the evolution equations for the parameters of the precipitates including the shape parameter. In contrast to the phase-field approach [7] our concept is based only on real physical quantities and well-defined geometry of objects. The model is used for the simulation of the precipitation kinetics of Ti_3AlN and Ti_2AlN in the Ti–Al–0.5 at.% N matrix, and the results of simulations are compared with experiments presented in the open literature.

2. Shapes of precipitates

Often spheroidal precipitates are observed with an equator radius a and the length αa of the half-axis of rotation, α denominates the aspect ratio. For an arbitrary a and α it is possible to find an equivalent cylindrical precipitate with the same volume and by inserting h_k for α. Then the diameter of the cylinder is given by $D_k = (16/3)^{1/3}a$.

Each cylindrical precipitate k can be described either by the height H_k and the diameter D_k or by the aspect ratio h_k and the equivalent radius ρ_k of the sphere of the same volume as that of the cylinder. The corresponding relations are

$$D_k = \beta_k \rho_k \tag{1}$$

$$H_k = \beta_k h_k \rho_k \tag{2}$$

For the time derivatives, marked by a dot, one finds

$$\dot{D}_k = \beta_k(\dot{\rho}_k - \rho_k \dot{h}_k/(3h_k)) \tag{3}$$

$$\dot{H}_k = \beta_k(h_k \dot{\rho}_k + 2\rho_k \dot{h}_k/3) \tag{4}$$

The reader should note that, in addition to concepts outlined in Refs. [1–4], we have now further time-dependent quantities h_k, the evolution equations for which must be added to the system of equations outlined in Ref. [4], Section 3.

3. Model

We assume that each precipitate k is described by its equivalent radius ρ_k, its average values of concentrations c_{ki} of components i in the precipitate and by its aspect ratio h_k.

3.1. Total Gibbs energy of the system

Similar to Refs. [1–4] the total Gibbs free energy G of a fixed amount of matter with n components and m precipitates can be expressed as

$$G = \sum_{i=1}^{n} N_{0i}\mu_{0i} + \sum_{k=1}^{m} \frac{4\pi\rho_k^3}{3}\left(\lambda_k(h_k) + \sum_{i=1}^{n} c_{ki}\mu_{ki}\right) + \sum_{k=1}^{m} 4\pi\rho_k^2 \cdot \frac{\beta_k^2}{8}\left(\gamma_k^H + 2h_k\gamma_k^D\right) \tag{5}$$

The first term is the chemical part of the Gibbs energy of the matrix, the second term corresponds to the stored elastic energy and to the chemical part of the Gibbs energy of the precipitates and the third term represents the total precipitate/matrix interface energy. The subscripts "0" denote quantities related to the matrix, e.g., N_{0i} is the number of moles of component i in the matrix and μ_{0i} its chemical potential in the matrix. The quantity $\lambda_k(h_k)$ accounts for the contribution of elastic strain energy due to the volume misfit between the precipitate and the matrix, and μ_{ki} are the values of chemical potentials in the precipitates corresponding to c_{ki}. We distinguish between the interface energy γ_k^D at the mantle of the cylinder and γ_k^H at the bottom and top of the cylinder.

There exists a well-elaborated concept to calculate the elastic strain energy due to a misfit eigenstrain in a spheroidal inclusion, going back to Eshelby's seminal work, see, e.g., Refs. [10,11]. The precipitate is geometrically defined by a and α. The elastic properties of the matrix are E (Young's modulus) and v (Poisson's ratio). We assume an elastic contrast C to the precipitates with the Young's modulus CE, and, for sake of simplicity, the same Poisson's ratio v. The misfit eigenstrain is characterized by the isotropic strain δ and an additional eigenstrain component $\Delta\delta$ in the direction of the axis of rotation of the spheroidal precipitate. Finally by inserting h_k for α the factor $\lambda_k(h_k)$ reads as

$$\lambda_k(h_k) = \frac{E\delta^2}{1-v}\left[F_0(h_k;\Delta C) + F_1(h_k;\Delta C)(\Delta\delta/\delta) + F_2(h_k;\Delta C)(\Delta\delta/\delta)^2\right] \tag{6}$$

with $\Delta C = C - 1$. The functions $F_0(h_k;\Delta C)$, $F_1(h_k;\Delta C)$ and $F_2(h_k;\Delta C)$ are found by evaluating the "Eshelby scheme" outlined in Refs. [10,11]. A constant Poisson's ratio $v = 0.3$ is used in Fig. 1a–c, where the reader can find the curves of the three functions. Furthermore, the F_0, F_1, F_2 can be approximated by $\log F_i = P_i(x) - \log(1 + \Delta C)$ with $P_i = A_i + B_i x + C_i x^2 + D_i x^3$ and $x = \log h_k$. The coefficients A_i, B_i, C_i, D_i are given in Table 1.