Modelling the role of compositional fluctuations in nucleation kinetics

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Abstract—The classical nucleation theory of precipitate nucleation in interstitial/substitutional alloys is applied to account for the influence of spatial A–B composition fluctuations in an A–B–C matrix on the kinetics of nucleation of $(A,B)_3C$ precipitates. A and B are substitutional elements in the matrix and C is an interstitial component, assumed to preferentially bind to B atoms. All lattice sites are considered as potential nucleation sites. The fluctuations of chemical composition result in a local variation of the nucleation probability. The nucleation sites are eliminated from the system if they are located in a C-depleted diffusion zone belonging to an already nucleated and growing precipitate. The chemistry is that of an Fe–Cr–C system, and the specific interface energy is treated as a free parameter. Random, regular and homogeneous A–B distributions in the matrix are simulated and compared for various values of the interface energy. An increasing enhancement of the role of compositional fluctuations on nucleation kinetics with increasing interface energy and decreasing chemical driving force is observed.
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1. Introduction

Precipitation is understood as the formation of particles of a new phase from a supersaturated solid solution. The first stage of precipitation is nucleation, usually described by classical nucleation theory (CNT) developed by Becker and Döring [1], which follows also from the solution of the Fokker–Planck equation derived by means of the cluster dynamics (CD) method; for details see, for example, Refs. [2–4]. Nucleation consists of the following periods:

(i) the incubation period, providing the necessary time for formation of the critical nucleus by diffusion of components to the nucleation centre;
(ii) the steady state nucleation period, during which the nucleation conditions and the nucleation rate change insignificantly;
(iii) the period during which the nucleation rate is decreasing due to exhaustion of potential nucleation sites and/or a decrease of the supersaturation of the matrix, causing a decrease of the driving force for nucleation.

The second stage of precipitation is the growth stage, followed by the third stage, which is coarsening [5,6].

It is also possible to model nucleation directly by the CD method, which allows treating the evolution of a single cluster or an ensemble of clusters in size space [7,8]. CD models assume that the size of a cluster fluctuates due to absorption and desorption of atoms from the surrounding matrix. Some CD studies of nucleation and growth of precipitates can be found, for example, in Refs. [9–11]. A study of critical nuclei, where also the composition dependence of the interface energy is accounted for, can be found, for example, in Ref. [12].

Atomistic Monte Carlo (MC) methods represent an alternative approach for studying precipitation [13–16]. Since the atomistic MC methods naturally include fluctuations of composition at the atomic level, they can give more detailed information about the initial stages of precipitation compared to CNT or CD methods. There exist, however, also some shortcomings in application of the MC technique to the modelling of precipitation. First, the system is usually described by a set of inter-atomic interaction coefficients, which do not allow a free choice of the interface energy between cluster and matrix. Second, there is obviously no clear definition of a cluster representing a precipitate in the nucleation or early growth stage [17]. If not stated explicitly, a cluster is usually considered as a confinement of atoms or molecules with at least one nearest neighbour connection. In the treatment based on CD, the cluster approximated by a sphere is well defined and the interface

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energy between cluster and matrix can be treated as a free parameter.

Of course, modelling makes it necessary to select a specific material system. The $(Cr,Fe)_3C$ carbide has been chosen as a prototype. This carbide represents also other Cr-rich carbides that nucleate in this alloy system as $(Cr,Fe)_7C_3$ or $(Cr,Fe)_{23}C_6$ [18]. These precipitates typically show a more or less pronounced enrichment in Cr, substituting the lattice-forming element Fe of the matrix. The more Cr the matrix contains in the initial state, the more Cr is usually found in the precipitates. Nevertheless, all of these carbides are often thermodynamically stable over the entire composition range from Cr-rich to Fe-rich carbides with a clear kinetic advantage for the Fe-rich precipitates with a composition according to para-equilibrium. In this case the slow Cr diffusion is not required and fast interstitial C diffusion is fully sufficient for nucleation. Then the fluctuations of the chemical composition in Cr can play a key role in nucleation kinetics, and this is the main motivation for the present study. The Fe–Cr–C system, however, serves only as an example of general substitutional-interstitial systems. That is why we generalize the further treatment in an A–B–C formulation. Furthermore, we assume that the nucleation process of the complex carbides mentioned above occurs due to clustering of interstitial C atoms in the crystal structure of the body centred cubic (bcc) matrix. The transformation of the bcc pre-cluster to the final orthorhombic structure of the $(A,B)_3C$ phase is assumed to occur subsequently without a significant delay. This scenario is supported by experimental evidence [19].

In the present paper, we apply CNT locally to each individual substitutional lattice site to study nucleation kinetics of the $(A,B)_3C$ phase in a random, regular or homogeneous A–B–C matrix with A, B being substitutional and C interstitial atoms. The substitutional A atoms are assumed to be the majority species, and the interstitial C atoms are assumed to energetically prefer B atoms. Simulations are performed on a system represented by a box of a bcc lattice with periodic boundary conditions. The arrangement of substitutional A and B atoms in the lattice is either random or regular. Both arrangements are compared with the case of a homogeneous matrix as in classical CNT, supposing that to each lattice site the same chemical composition corresponding to the average composition of the matrix is attributed. Interstitial C atoms are treated on a continuum basis, in order to avoid too high computational effort. To each lattice site, local conditions for nucleation are associated. Para-conditions for nucleation are assumed, which imply that substitutional atoms are immobile; see, for example, Ref. [20]. To account for the influence of the already nucleated and grown precipitates, all lattice sites are excluded as potential nucleation sites, if they are located in the diffusion zones of growing precipitates.

The aim of this paper is to show, within the framework of CNT, how the random spatial fluctuations of A, B atoms affect the nucleation of the $(A,B)_3C$ phase in dependence on interface energy and chemical composition of the alloy. The results of the treatment are compared with those calculated for a regular and homogeneous matrix. This original study provides clear evidence for the role of compositional fluctuations in substitutional elements on the nucleation kinetics. The effect of fluctuation itself on the nucleation kinetics drastically increases with increasing interface energy.

2. Classical nucleation theory

According to CNT (see, for example, Refs. [2,3]), the nucleation rate J can be expressed as

$$\frac{dN}{dt} = J = J^{SS} \exp\left(-\frac{\tau}{t}\right) \frac{N_0 - N}{N_0}, \tag{1}$$

where N is the number of nucleated precipitates, J^{SS} is the steady-state nucleation rate, t is the time, τ is the incubation time and N_0 is the number of potential nucleation sites for precipitates. The steady-state nucleation rate can be written as

$$J^{SS} = \beta^* N_0 \exp\left(-\frac{G^*}{kT}\right), \tag{2}$$

where G^* is the Gibbs energy barrier to form a critical nucleus (later nucleation barrier), k is the Boltzmann constant and T is the absolute temperature. For spherical precipitates, the nucleation barrier G^* in Eq. (2) is formulated as

$$G^* = \frac{16\pi}{3} \frac{\gamma^3}{\Delta F^2}, \tag{3}$$

where γ is the specific interface energy and ΔF is the total chemical and mechanical driving force. The radius ρ^* of the critical nucleus can then be written as

$$\rho^* = \frac{2\gamma}{\Delta F}. \tag{4}$$

The Zeldovich factor Z in Eq. (2) is tacitly assumed to be $Z = 1$. Here we refer to a text passage in the discussion, estimating the actual values of Z and discussing its role. The attachment rate β^* in Eq. (2) is expressed for a multicomponent system according to Ref. [21] as

$$\beta^* = \frac{4\pi \rho^{*2}}{a^4} \left[\sum_{i=1}^{m} \frac{(Y_i^P - Y_i^M)^2}{Y_i^M D_i^M} \right]^{-1}, \tag{5}$$

where a is the interatomic distance, m is the number of components in the system (in our case 3), Y_i^P (Y_i^M) is the site fraction of element i in the nucleus of a precipitate (matrix) and D_i^M is the diffusivity of element i in the matrix.

3. Evaluation of the local nucleation conditions

3.1. Determination of the local nucleation barrier

Let the system be represented by a cubic simulation box of a bcc crystal lattice, fully occupied by A and B atoms, with periodic boundary conditions. The A and B atoms are assumed to be distributed randomly or regularly at the lattice sites in the box. The random distribution mimics the actual spatial fluctuations of the chemical composition. The fluctuations cause different precipitate nucleation conditions at different lattice site positions in the box. Each precipitate can be considered as a cluster of A, B, C atoms of chemical composition $(A,B)_3C$ with its centre at a certain lattice site p. We define a nucleus as a subcritical precipitate with the radius $\rho < \rho^*$. The ratio of the number of substitutional atoms to the number of interstitial atoms in the cluster is fixed at 3:1. The size of a cluster is defined by the number n_C of interstitial atoms in the cluster. A set of virtual clusters of size $n_C = 1,2,3,\ldots$, can be addressed to each lattice site p.