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Formation and self-organization of void superlattices under irradiation: A phase field study

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ABSTRACT

Self-organized patterns, realized in non-equilibrium processes, have been widely observed in physics and chemistry. As a powerful tool to create far-from-equilibrium environments, irradiation produces a variety of types of defects, which can self-organize through physical interactions and chemical reactions. Such a process becomes complicated especially when both thermodynamics and kinetics play critical roles in pattern formation. In this paper, we investigate the formation and self-organization mechanism of void superlattices in metals and alloys under irradiation through phase field modeling and simulations. For the first time, three different formation mechanisms of void superlattices are clearly distinguished according to their thermodynamic origin and reaction kinetics. It is found that the characteristic length and symmetry of an emerging superlattice is determined by the interplay of the thermodynamic driving force and the kinetic anisotropy of the system. Through parametric study, the effects of kinetic coefficients, such as atomic mobility and irradiation dose rate, on the nucleation, growth, coarsening, coalescence, and ordering of voids are systematically investigated. The theoretical model developed in this work may provide guidelines for designing desired self-organized microstructures under irradiation.

1. Introduction

Self-organization phenomena occur in a number of different fields, including physics, chemistry and biology, and they have attracted intense research interest. The spontaneous ordering processes during self-organization usually occur in open and complex systems that are at non-equilibrium states. Typical self-organization in physics includes phase transitions, such as ferroic (ferroelastic, ferroelectric, ferromagnetic) phase transitions, classical crystal growth, and Bose-Einstein condensation [1–6]. In literature, it is well known that the ordering and self-organization during phase transitions are directly associated with spontaneous symmetry breaking. For example, ferroelastic/ferroelectric/ferromagnetic domains are self-organized during phase transitions, and the formation of multi-domain structures is dictated by the minimization of long range interaction energies (elastic/electrical/magnetic energies). Note that both characteristic length and symmetry appear during such spontaneous ordering processes [7,8]. The characteristic length is determined by the interplay between the domain boundary energy and the long range interaction energy of a system, while the characteristic symmetry is determined by the broken symmetry. In other words, the self-organization during phase transitions is dominated by thermodynamics (or energetics). Similarly, a few modeling methods, such as the atomic density function theory and phase field crystal model, are developed to capture the atomic level characteristic length and symmetry (i.e., lattice parameter and crystal symmetry) [9–12]. In these methods, the free energy is formulated as a functional of atomic densities, which includes both short-range and long-range thermodynamic interactions [9,11–14]. In contrast, the ordering and self-organization in reaction–diffusion systems in chemistry are usually dominated by kinetics (dynamics) [15–17]. In the Turing instability, for example, the ordering is dictated by the dynamic coupling between two (or more) components, which originates from chemical reactions. The competition between different temporal rates and spatial ranges of diffusion for different components is critical for the occurrence of dynamic instability. A characteristic length emerges in such a reaction–diffusion process, which is determined by the interplay of kinetic coefficients (e.g., diffusivity) and reaction terms. In addition, if the kinetic coefficients or reaction terms are associated with anisotropy (or symmetry breaking), characteristic symmetry is also expected during self-organization. Even though the above two different kinds of self-organizations may be distinguished in terms of thermodynamics and kinetics, real systems with both mechanisms involved could exit, especially in complex environments.

Irradiation is a powerful means to create complex environments and develop self-organized defect structures. On the one hand, as a continuous external stimulus maintains the system at states far from equilibrium, a large number of lattice defects of either vacancy or self-interstitial-atom (SIA) type are generated during irradiation. These defects can be either isolated such as individual vacancies or SIAs, or

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agglomerate to form such as clusters and loops, etc. Along with these lattice defects, incorporation of impurities introduced by the implanting particles including ions and neutrons is possible. On the other hand, the internal interactions and reactions among those defects are activated, leading to the accumulation, annihilation, and organization of defects. Typical examples include dynamically-driven compositional patterning [18], the ordering of defect clusters and loops, and void and gas bubble superlattices in pure metals and alloys [19–23]. In general, self-organization under irradiation takes place as a result of the competition between the kinetics that drives the system towards equilibrium and the external stimuli that keep the system far from equilibrium. Such a competition has been well understood for the case of nanoscale compositional patterning [18]. However, a good understanding of void and bubble superlattices has yet to be established. In literature, several different theoretical approaches have been proposed to understand void superlattice formation. Parallel to phase transition and spinodal decomposition in solid and liquid solutions [24], thermodynamic descriptions of void formation have been suggested by Malen and Bullough [25], Imada [26] and Veshchunov and Matveev [27], with however incomplete descriptions of defect production, reaction and annihilation. For instance, in Malen and Bullough [25], the void superlattice is regarded as a result of anisotropic elastic interactions among voids, without contributions from kinetic aspects. Although the elastic anisotropy could lead to ordering of voids, as indicated by 2D phase field simulations [28], the symmetry selection in 3D cases is not clear. In particular, the nucleation mechanism and development of superlattices in elastically isotropic tungsten cannot be well understood. Dynamic instability analysis based on the so-called rate theory is another popular approach that has been widely adopted in literature [29–32]. Rate theory captures the dynamic nature of the production, annihilation, and reactions of SIAs and vacancies as well as their agglomerates. However, a term analogous to Fickian diffusion is usually used for mass transport in this kind of analyses, and thus the thermodynamic origin of void formation is overlooked. In rate theory, the vacancy diffusion is driven by a concentration gradient. In contrast, the void formation in reality is through a diffusion against the concentration gradient, i.e., the diffusion is driven by the chemical potential gradient. As a consequence, the link between void formation and thermodynamic materials properties cannot be captured in rate theory. Theoretically, an analysis coupling both thermodynamics and kinetics is desired in the investigation of void lattice organization [33]. In particular, the pattern formation in self-organization could be related to the anisotropic diffusion of SIAs [33–39] or their clusters such as loops [40]. In fact, even without elastic anisotropy, 1D SIA diffusion is able to cause bubble superlattice formation, where a high ratio between the diffusivities of SIA and vacancy is suggested by 2D phase field simulations [38]. In addition, the role of 1D SIA diffusion in void superlattice formation has been further confirmed by atomic kinetic Monte Carlo (AKMC) simulations recently in both BCC and FCC crystals. It has been found that void superlattices can form as a result of spinodal decomposition of voids from the matrix, during which a characteristic length develops, with the simultaneous symmetry development dictated by the directions of SIA diffusion [33]. As the governing kinetics for the phase separations and defect reactions are different, i.e., the former by mass transport and the latter by the mutual recombination, the developments of characteristic length and symmetry of superlattices can occur at different stages. Prior to the present work, it has not been clearly demonstrated how these competing kinetics will affect the superlattice formation, and how the superlattice symmetry is determined at the continuum scale. Both of the above issues are the focus of this study.

In this work, we propose a model incorporating both the thermodynamic origin and the kinetic reactions during void superlattice formation under irradiation. By incorporating gradient thermodynamics and a Cahn–Hilliard type diffusion equation [41], a phase field model is developed to investigate the formation and evolution of void superlattices. A new scheme capturing the 1D SIA diffusion is proposed, without the calculations of the interstitial probability as in previous study [38]. The new approach is straightforward to implement in 2D and 3D with arbitrary anisotropy in SIA diffusion. As two examples, BCC and FCC types of void superlattices in 3D are obtained in phase field simulations. Consistent with previous studies, it is found that the characteristic length (related to the lattice parameter of the superlattice) is determined by an intrinsic thermodynamic instability influenced by the reaction kinetics, and the superlattice symmetry is dictated by the anisotropic diffusion of SIAs. Moreover, the competing kinetics for phase separation and defect reactions lead to three different formation mechanisms of void superlattices. By combining phase field simulations and theoretical analysis, a diagram capturing the selection of superlattice formation mechanisms is built with regards to irradiation conditions (e.g., dose rate) and reaction kinetics (e.g., mutual recombination).

2. Methodology

As mentioned above, both vacancy and SIA types of defects are generated in metals and alloys under irradiation. Depending on the size and configuration they take (point and cluster defects), these defects can be further divided into numerous types, and each type requires a rate equation to describe its evolution, similar to what has been done in previous instability analyses [31,32,40]. To simplify the theoretical analysis, we here identify the minimum number of essential factors that may be needed for void superlattice formation. To form voids, vacancy supersaturation in the matrix is necessary, which in turn needs defect production, transport, as well as the annihilation by recombination and sink absorption. A thermodynamic description of vacancies in the matrix and voids is needed as well. To simulate recombination, the evolution of SIAs needs to be considered, with its anisotropic diffusion governing the symmetry developed during phase separations. Following the mean field description, only the concentrations of vacancies and SIAs are considered in our theoretical model, which are the minimum factors required for void superlattice formation. The evolution of time- and spatially-dependent concentrations, c_v and c_i for vacancies and SIAs, respectively, are given by:

$$\frac{\partial c_v}{\partial t} = \nabla \cdot M_v \nabla \left(\frac{\delta F}{\delta c_v} \right) - K c_v \sum_{i=1}^{n} c_i + P_v + \xi_v \tag{1}$$

$$\frac{\partial c_i}{\partial t} = \nabla \cdot D_i \nabla c_i - K c_v c_i + P_i + \xi_i, \; i = 1, 2, ..., n \tag{2}$$

Here subscripts v denote vacancy, and $i = 1, 2, ..., n$ denote the ith type of SIAs. P_v and P_i are the production rates (related to the dose rate). M_v and D_i denote the atomic mobility of vacancies and the diffusivity of SIAs, respectively. F is the total free energy of the system. K is the reaction rate for recombination. In Eq. (1), we further ignore sink absorption in its isotropic form, which could affect vacancy accumulation rate but not significantly the competition between phase separation and mutual recombination. The reaction rate for recombination is reduced to a constant K to better elucidate the competing kinetics. In reality it is given by $K = \frac{4\pi R_{iv}(D_i + D_v)}{\Omega}$, where R_{iv} is the recombination radius, D_v is the vacancy diffusivity, and Ω is the atomic volume. ξ_v and ξ_i are Langevin noise terms simulating fluctuations in vacancy and SIA concentrations, which meet the fluctuation-dissipation theorem.

Our model couples the rate theory for production and reaction kinetics [42], and the Cahn–Hillard approach for the phase separation description of void formation [24,28]. In phase field model, a void is described as a new “phase”, the formation of which is the result of vacancy diffusion and accumulation [38,43–54]. In addition, n types of SIAs are introduced in our new approach, each of them diffusing anisotropically along a particular crystallographic direction, which could be related to the symmetry of the host matrix. For example, in a BCC host matrix, if the SIAs diffuse in 1D along ⟨111⟩, there are four types of SIAs ($n = 4$), which diffuse along [111], [11$\bar{1}$], [1$\bar{1}$1], [$\bar{1}$11], respectively. In an FCC host matrix, if the SIAs diffuse in 1D along ⟨110⟩, there are six types of SIAs