Computational Materials Science 106 (2015) 111–122

Contents lists available at ScienceDirect

Computational Materials Science

journal homepage: www.elsevier.com/locate/commatsci

A defect-based model of radiation-induced segregation to free surfaces in binary alloys

Santosh Dubey *, Anter El-Azab

School of Nuclear Engineering, Purdue University, West Lafayette, IN, USA

ARTICLE INFO

Article history:
Received 3 January 2015
Received in revised form 1 April 2015
Accepted 28 April 2015
Available online 16 May 2015

Keywords:
Radiation-induced segregation
Radiation effects
Reaction–diffusion system
Modeling and simulation

ABSTRACT

A defect-based model of radiation-induced segregation in binary solid solutions is presented. The model consists of a set of reaction–diffusion equations governing the space and time evolution of vacancies, dumbbell interstitials and lattice atoms under irradiation. Irradiation, the mechanism driving evolution, is represented by stochastic and spatially-resolved defect generation events. A key feature of the model presented here is that the role of boundaries as defect sinks is ensured by a set of defect–boundary reaction boundary conditions. Defining defect–boundary interactions in this way makes it possible to capture both segregation and boundary motion simultaneously. The model is tested with Cu–Au solid solution. Enrichment of Cu and depletion of Au has been observed near the boundaries, in agreement with experimental observations. For a particular dose rate, the amount of segregation after a given period of irradiation has been found to be highest at an intermediate temperature. At lower temperatures, maximum segregation is observed by lowering the dose rates, and vice versa. The activation barrier for the defect–surface reactions plays a significant role in segregation near the boundaries. A slight increase in the sample size is also noticed during the simulations due to rapid migration of interstitials to the surface.

1. Introduction

Radiation-induced segregation (RIS) in alloys results in changes in the chemical environment near extended defects like surfaces and interfaces, which has important consequences. For instance, in nuclear reactor, the depletion of Cr near grain boundaries in austenitic stainless steels (Fe–Cr–Ni alloys) under irradiation is a mechanism of susceptibility to inter-granular fracture by irradiation-assisted stress corrosion cracking [1]. RIS is a non-equilibrium phenomenon that also affects the diffusional and clustering behavior of the defects, thereby influencing almost all the kinetic processes and material properties in nuclear reactors.

Several models have been proposed to study RIS in concentrated alloys based on the concept of inverse Kirkendall effect (IKE) [2]. These models may be classified into two classes based on the way diffusion is modeled. The first class of the models employs a continuum approach to formulate diffusion in the framework of random alloy theory of Manning [3]. Models by Wiedersich [4], Marwick [2], Lam and Wiedersich [5], and Perks and Murphy [6] belong to this category. In Manning's model, diffusion is based on vacancy mechanism; its extension to systems under irradiation [2–6], where vacancies and interstitials are present in equal proportions, is done in such way that they do not contribute to segregation. With this premise it was difficult to explain the segregation of various components in Fe–Cr–Ni alloy to the grain boundaries [7]; the degree of Ni enrichment near the grain boundaries did not increase when Ni was increased from 15% to 35%, and the degree of Cr depletion was found to be insensitive to the chromium content. On the contrary, the models in [2–6] predicted that nickel enrichment or chromium depletion at the grain boundaries should increase with nickel and chromium concentrations, respectively. This anomaly was later resolved by Murphy [8] when he proposed a model for multi-component systems under irradiation in which contribution of the interstitials to RIS was also considered. Interstitial contribution to RIS was explained by introducing a coupling between an interstitial and a lattice atom during the diffusion of dumbbell interstitials. Such a coupling was observed by conversion of interstitials type via lattice atom mediation. Hashimoto [9] simplified Murphy's model for a binary system, and included change in the dumbbell type reactions in addition to the dumbbell diffusion. In all the models mentioned above, the defect and atomic migration barriers are assumed to be independent of the local environment. Using the method developed by Grandjean [11], Allen and Was [10] proposed a model in which the migration barriers were dependent on the local atomic concentration.

* Corresponding author at: Department of Physics, University of Petroleum & Energy Studies, Dehradun, UK, India.

http://dx.doi.org/10.1016/j.commatsci.2015.04.040
0927-0256/

The other class of models, proposed by Grandjean [11], relies on a mean-field type treatment of diffusion on a discrete lattice using rate theory [12]. In this framework, since the description of diffusion is atomistic, the effect of composition and short range ordering on segregation is automatically taken care of. The treatment of interstitials diffusion has been very simplified in this work: the difference in the migration energies of various interstitial configurations has not been considered. Therefore, the interstitial contribution to RIS is not visible. This model, therefore, may not be used in systems where irradiation produced interstitials form dumbbells, and interstitials contribution is important in predicting overall segregation behavior. However, in a series of articles by Nastar et al. [13,14], the discrete lattice rate theory has been extended to the split-interstitial diffusion mechanism to explain the role of interstitials on radiation-induced segregation.

All the models employing continuum theory of diffusion have been solved on 1D domain with the boundary condition that the surface is always maintained at bulk thermal defect concentration. This is not an issue in discrete lattice theory models, as mentioned earlier, because in these models not only the surface point defect concentration is varying with time in accordance with the concentration of alloying components but also its value at equilibrium does not coincide with the equilibrium bulk value [11,12]. Now the question arises: should RIS be studied in higher dimensions or 1D study is sufficient to understand the overall effect of RIS on materials? In materials with internal defect sinks, e.g., voids, dislocation loops, grain boundaries, etc., RIS affects the chemical environment near the defect sinks which leads to alteration in the evolution (growth and shrinkage) of these sinks. Such microstructures features inherently have 3D morphologies and to resolve chemical changes near them, a 3D treatment of RIS is required. In the case of free surface, studying RIS in higher dimensions may help capture intricate details of the process such as the role of the surface motion in RIS, spatial non-uniformity of segregated species near the surface, and surface roughening due to defect–surface interactions.

Here we propose a model to study RIS near free surfaces in binary solid solutions. This model applies to materials where irradiation-produced interstitials form dumbbells. For a binary system under irradiation (AB), the model tracks the space and time evolution of six species: three off-lattice species (AA, BB and AB dumbbells), and three on-lattice species (A, B lattice atoms, and vacancy). The dumbbells diffuse via interstitialcy mechanism [15], whereas vacancies diffuse via vacancy mechanism. The defect diffusion fluxes are derived using a continuum approach, and the diffusion of atoms is coupled to that of the defects. The defects also participate in two types of reactions: recombination of interstitial dumbbells with vacancies and dumbbell type conversion. Point defect generation is modeled by collision cascade events. These events are discrete and stochastic in space and time. In each event, a random amount of defects is introduced as the final outcome of a spatially-resolved small cascade: vacancies are distributed in a bell-shaped profile at the cascade center, whereas interstitials are distributed in a ring-shaped profile at the cascade periphery. The evolution of all the species is tracked by solving a system of coupled non-linear reaction–diffusion equations. The role of the surface as a defect sink has been ensured by a reaction boundary condition, which quantifies the rate of reaction of defects with the surface. The surface motion is estimated by invoking mass balance across the surface. The model has been employed to study RIS in Cu–Au solid solution in 2D (solution in 3D is straightforward). In addition to being able to reproduce essential trends of RIS in Cu–Au solid solution presented elsewhere by other authors [9], this model has been able to provide additional insights into the RIS process in general and its dependence on the surface motion in particular.

In Section 2, we present the reaction–diffusion model [19], including the reaction boundary conditions. A discussion of the numerical scheme adopted for approximating the model equations with a moving boundary follows in Section 3. Section 4 includes the model results describing segregation and defect dynamics near the free surfaces in Au–10%Cu solid solution under irradiation. Conclusions are drawn in Section 5.

2. Radiation-induced segregation model development

2.1. Model equations

In a concentrated binary solid solution, AB, subjected to irradiation, we focus mainly on the defect dynamics, while changes in the local concentration of the alloying components follow from the processes of defect generation, diffusion and reactions. Since defects are always present in dilute concentrations, even under irradiation, the effect of their interaction on the overall response of the system may be safely discounted, and as such a Fickian treatment of the diffusion becomes equivalent to a chemical one. For this treatment to be precise, however, the effect of the local composition on the diffusion kinetics of point defects must be taken into consideration, which we do not consider here due to a lack of atomistic data. There are six species in the model: three types of dumbbell interstitials (AA, BB and AB), vacancy, A and B lattice atoms. The defects are assumed to be sufficiently mobile in the temperature range considered here. The dumbbell interstitials diffuse via interstitialcy mechanism [15], whereas vacancies diffuse via vacancy mechanism. Diffusion of the atoms is coupled to the diffusion of defects. In addition to long-range diffusion, defects also participate in two types of reactions: a dumbbell interstitial may recombine with a vacancy to give rise to two lattice atoms, and it may also react with a lattice atom to undergo a change in the dumbbell type reaction. Evolution of all the species is governed by a reaction–diffusion type dynamics with stochastic, spatially-resolved defect generation term $\widehat{S}$.

The governing equations have the following form:

$$\frac{\partial C_{AA}}{\partial t} = -\nabla\cdot(\Omega J_{A^{\rightarrow}}(\mathrm{AA})) - R^{v}_{AA} + Q^{AA} + \widehat{S}^{casc}_{AA} \tag{1a}$$

$$\frac{\partial C_{BB}}{\partial t} = -\nabla\cdot(\Omega J_{B^{\rightarrow}}(BB)) - R^{v}_{BB} + Q^{BB} + \widehat{S}^{casc}_{BB} \tag{1b}$$

$$\frac{\partial C_{AB}}{\partial t} = -\nabla\cdot(\Omega[J_{A^{\rightarrow}}(\mathrm{AB}) + J_{B^{\rightarrow}}(\mathrm{AB})]) - R^{v}_{AB} + Q^{AB}_{A^{\rightarrow}} + Q^{AB}_{B^{\rightarrow}} + \widehat{S}^{casc}_{AB} \tag{1c}$$

$$\frac{\partial C_{v}}{\partial t} = -\nabla\cdot(\Omega J_{v}) - R^{v}_{AA} - R^{v}_{BB} - R^{v}_{AB} + \widehat{S}^{casc}_{v} \tag{1d}$$

$$\frac{\partial C_{A}}{\partial t} = -\nabla\cdot(\Omega J_{A}) + R_{A} + Q^{A} + \widehat{S}^{casc}_{A} \tag{1e}$$

$$\frac{\partial C_{B}}{\partial t} = -\nabla\cdot(\Omega J_{B}) + R_{B} + Q^{B} + \widehat{S}^{casc}_{B} \tag{1f}$$

where $J_i = \sum_k D_{ik}\nabla C_k$ and R_i are the flux and reaction terms of ith species (i, k = AA, BB, AB, V, A, B), respectively, D_{ik} is a $M \times M$ matrix of concentration-dependent diffusion coefficients, M is the number of species in the model, and C_k is the fractional concentration of kth species; Q represents change in the dumbbell type reaction; Ω is atomic volume. All the terms in the right hand side of the above Eqs. ((1a)–(1f)) have been derived elsewhere [19]. The stochastic nature of the $\hat{S}$ terms renders the partial differential equation system above stochastic.