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Multiscale modeling of Radiation Induced Segregation in iron based alloys

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ABSTRACT

In metallic alloys of fission or fusion reactors, microstructural evolution results from a dynamic equilibrium between thermodynamic forces and the production of defects by irradiation. The migration of defects can lead to the formation of clusters of defects (nano-cavities, dislocation loops, nano-precipitates) or variations in chemical composition close to the defect sinks, a phenomenon known as Radiation Induced Segregation (RIS). To predict the effect of irradiation conditions (type of irradiation particle, dose rate, temperature), phenomenological diffusion models exist that have to be assembled to give an overall description. Our objective is to describe these models and to propose numerical implementations to solve them starting at the atomic scale (DFT energy calculations, Kinetic Monte Carlo, Self-Consistent Mean Field approaches) to reach the mesoscopic one using the phase field modeling. This multi-scale approach is illustrated by a short review of recent studies focusing on dilute and concentrated iron based alloys.

1. Introduction

Radiation induced segregation (RIS) is a non-equilibrium segregation process that was first predicted by Anthony [1] in the late 60s. The irradiation of metallic materials produces vacancies and self-interstitial atoms (SIAs) by elastic collisions between the incoming particles and the atoms of the target. These point defects (PDs) subsequently migrate by thermally activated jumps and may annihilate by mutual recombination, cluster or eliminate at point defect sinks such as dislocations, grain boundaries, free surfaces, etc. The balance between the creation and elimination mechanisms may result in PD concentrations far above the equilibrium values, and to net fluxes of PD toward sinks.

In pure metals, the evolution of the spatial average PD atomic fractions can be analyzed by means of homogeneous rate equations

$$\begin{aligned} \frac{d\overline{X}_V}{dt} &= K_0 - R\overline{X}_V\overline{X}_I - \sum_s k_{sV}^2 D_V(\overline{X}_V - X_V^s) \\ \frac{d\overline{X}_I}{dt} &= K_0 - R\overline{X}_V\overline{X}_I - \sum_s k_{sI}^2 D_I(\overline{X}_I - X_I^s) \end{aligned} \tag{1}$$

where K_0 is the rate of creation (in dpa s^{-1}), $R = 4\pi r_c(D_I + D_V)/V_{at}$ the rate of recombination (with r_c the distance of recombination, D_I and D_V the PD diffusion coefficients and V_{at} the atomic volume). X_V^s and X_I^s are the PD atomic fractions at sinks, where they are considered to be sustained at their equilibrium values (X_V^{eq} and X_I^{eq}), or when appropriate put equal to zero. k_{sV}^2 and k_{sI}^2 are the sink strengths of the various sinks s. Analytical expressions of the sink strengths for dislocations, thin films, etc., have been obtained by solving diffusion equations [2] assuming simplifying boundary conditions. Note that a good estimation of the sink strength is especially crucial for the modeling of void swelling, which is related to the dislocation bias

$$B_d = \frac{k_{dI}^2 - k_{dV}^2}{k_{dI}^2}, \tag{2}$$

mostly sensitive to the elastic interactions between dislocations and point defects.

In alloys, fluxes of PD give rise to fluxes of the chemical elements, leading to RIS: a local modification of the alloy composition near sinks. In an A-B alloy, the evolution of the position-dependent solute and PD atomic fractions are given by the following diffusion equations [3]

$$\begin{aligned} \frac{\partial X_V}{\partial t} &= -V_{at}\mathrm{div}J_V + K_0 - RX_VX_I - K_V^{abs} \\ \frac{\partial X_I}{\partial t} &= -V_{at}\mathrm{div}J_I + K_0 - RX_VX_I - K_I^{abs} \\ \frac{\partial X_B}{\partial t} &= -V_{at}\mathrm{div}J_B. \end{aligned} \tag{3}$$

The first two equations correspond to Eqs. (1) where the divergence of fluxes and the spatial variation of the atomic fractions are neglected. K_V^{abs} and K_I^{abs} are the local PD absorption rates, as explained in Section 4.2.

According to the thermodynamics of irreversible processes, the

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fluxes of PD and solute are given by:

$$J_\alpha = -\sum_\beta L_{\alpha\beta}\frac{\nabla\mu_\beta}{k_B T}, \tag{4}$$

where $\nabla\mu_\beta$ is the gradient of chemical potential of species β, k_B the Boltzmann constant, T the temperature and $L_{\alpha\beta}$ the Onsager or phenomenological coefficients. The same fluxes can be given in terms of partial diffusion coefficients and gradients of concentration. However, Eq. (4) highlights the actual driving forces $\nabla\mu_\beta$ and the Onsager coefficients, which give a direct indication of the sign of flux couplings: e.g. the fluxes of B and V are in opposite direction if L_{BV} is negative and in the same direction otherwise. Wiedersich et al. have shown [4] that in the steady state, in the vicinity of a point defect sink, the gradients of B and V are related by:

$$\nabla X_B = -\frac{L_{AV}L_{AI}}{L_{AI}D_B + L_{BI}D_A}\left(\frac{L_{BV}}{L_{AV}}-\frac{L_{BI}}{L_{AI}}\right)\frac{\nabla X_V}{X_V} = \alpha\frac{\nabla X_V}{X_V}, \tag{5}$$

where D_A and D_B are the intrinsic diffusion coefficients of A and B (which are a combination of Onsager coefficients and first derivatives of chemical potentials, with respect to PD and atomic fractions). One observes a depletion of solute near the sink when $\nabla X_B/\nabla X_V > 0$, an enrichment otherwise. It is clear that a predictive modeling of RIS requires a reliable description of both the chemical potentials and the Onsager coefficients. The later are very difficult to measure experimentally (especially those of self-interstitials), but recent progress in first-principles methods makes them relatively easy to compute from the migration barriers and jump frequencies of PD in pure metals and alloys.

Several strategies are possible to predict RIS. The first one is to develop diffusion and random-walk models to make the link between the jump frequencies and the Onsager coefficients. The task is far from trivial, due to the correlations between successive PD jumps. Nevertheless, recent progress has been made, especially in dilute alloys, thanks to the development of new mean-field models. For example, systematic estimations of Onsager coefficients in Fe-X alloys are now available and are presented in Section 2. Such analytical approaches are important to analyze the detailed mechanisms of coupling that control the RIS. Alternatively, atomistic kinetic Monte Carlo (AKMC) methods can be used with the same PD diffusion model, to measure the same transport coefficients but also to simulate the evolution of concentration profiles. AKMC simulations are especially useful for concentrated alloys, where the analytical expressions of Onsager coefficients are still based on more stringent approximations, and to simulate the evolution of concentration profiles near PD sinks with various geometries and densities. Another advantage of Monte Carlo methods is that they are also suited to the modeling of nucleation phenomena, and are therefore useful to study radiation induced precipitation. AKMC methods are presented in Section 3. They are nevertheless very time consuming and limited to small systems. Phase Field models are more appropriate to deal with large systems – but require a careful parametrization on AKMC results. Moreover, Phase Field models can include elastic interactions and provide precise calculations of sink strengths. They are presented in Section 4. To illustrate the combination of these different approaches, we will focus on the case of Fe-based binary alloys, and mainly on Fe-Cr alloys which are of great technological importance as a model for ferritic steels, and have been systematically studied in references [5–9].

2. Jump frequencies and transport coefficients

The jump frequency of a point defect in a given atomic environment can be computed in the framework or the transition state theory, using ab initio calculations. In dilute alloys, only a few environments have to be considered and all the relevant jump frequencies can be estimated by this method. In concentrated alloys there are many more possible configurations and simplified models must be used. RIS trends can then be predicted by estimating the transport coefficients $L_{\alpha\beta}$ and $D_{A,B}$ of eq. (5), using analytical diffusion models or AKMC simulations.

2.1. Atomic jump frequencies

Vineyard's harmonic transition state equation [10], gives the exchange frequency between, for example, a vacancy and a neighboring atom A:

$$\Gamma_{AV} = \nu_{AV}\exp\left(-\frac{\Delta G_{AV}}{k_B T}\right) = \nu_{AV}\exp\left(\frac{\Delta S_{AV}}{k_B}\right)\exp\left(-\frac{\Delta H_{AV}}{k_B T}\right) \tag{6}$$

where ΔH_{AV} is the migration enthalpy at constant pressure (or energy at constant volume), ΔS_{AV} the migration entropy and ν_{AV} the attempt frequency. ΔH_{AV} corresponds to the increase of the total enthalpy when atom A goes from its initial site on the crystal lattice (H_i) to the saddle point between its initial and final position (H_{SP}). Both the migration enthalpy and the prefactor $\nu_{AV}\exp(\Delta S_{AV}/k_B)$ depend on the local atomic configuration surrounding the PD. A similar expression holds for self-interstitials, which may adopt several configurations and migration mechanisms. DFT studies on self-interstitial properties – for which few experimental data are available – are of particular interest. The most probable configuration is predicted to be the [1 1 0] dumbbell in bcc iron and the [1 0 0] dumbbell in most fcc alloys [11,12].

The migration enthalpies are usually computed at 0 K by means of the drag or the nudged elastic band methods [13]. The vibrational formation and migration entropies are computed by means of a phonon calculation combined to a harmonic (or quasi-harmonic) approximation [10]. Another approximation is to consider only the phonon modes associated with the displacements of the hopping atom [14–16]. Knowledge of finite temperature effects is still incomplete: direct calculations of free energies beyond the harmonic approximation are scarce and applied to defect-free systems only [17], and the modeling of magnetic transitions and their effect on jump frequencies is mostly phenomenological [9,15,18–20].

In the dilute limit, a local environment is uniquely defined by the distance between the PD and the single solute atom, while in concentrated alloys the number of local configurations to be considered may become very large. DFT methods are still too time consuming to allow a full estimation of the migration barriers for all the possible configurations in concentrated alloys. The migration barriers ΔH_{AV} can be computed using various "broken-bond" models, where the enthalpy of atomic distributions on a perfect lattice are written as a sum of effective interactions. The results presented in Sections 3 and 4 are based on this approach. The simplest models use constant pair interactions but a realistic description of the energetic landscape often requires N-body interactions deduced from a cluster expansion of ab initio formation energies [21], or concentration dependent interactions [6,9]. Some models assume a linear dependence between the saddle-point enthalpy (H_{SP}) and the enthalpies of the system after (H_f) and before (H_i) the jump: $H_{SP} = (H_f + H_i)/2 + Q$ (which comes down to choosing an average migration barrier, Q). Others explicitly introduce effective interactions at the saddle-point [3]. The entropic contributions ΔS_{AV} and the effect of magnetic transition can be taken into account by the temperature dependence of the effective interactions [9]. Parameters of these models are fitted to experimental thermodynamic and diffusion data and/or DFT ordering energies and migration barriers. The use of experimental data is precious when finite temperature effects – such as the entropy contributions and the temperature-dependent magnetic interactions – have to be taken into account.

Alternatively, the jump frequencies can be measured by molecular dynamics (MD) [22–24], which naturally take into account finite temperature effects. However the method is limited to high temperatures and small migration barriers (i.e. interstitial diffusion). Moreover MD simulations usually use semi-empirical potentials and developing