



Full length article

## Modeling radiation induced segregation in iron–chromium alloys



Oriane Senninger<sup>a, \*</sup>, Frédéric Soisson<sup>a</sup>, Enrique Martínez<sup>b</sup>, Maylise Nastar<sup>a</sup>,  
Chu-Chun Fu<sup>a</sup>, Yves Bréchet<sup>c</sup>

<sup>a</sup> CEA, DEN, Service de Recherches de Métallurgie Physique, F-91191 Gif-sur-Yvette, France

<sup>b</sup> Los Alamos National Laboratory, Los Alamos, NM 87545, USA

<sup>c</sup> SIMAP, INP Grenoble, CNRS UJF, Saint Martin d'Hères Cedex, France

### ARTICLE INFO

#### Article history:

Received 2 March 2015

Received in revised form

25 September 2015

Accepted 29 September 2015

Available online xxx

#### Keywords:

Fe–Cr alloys

Monte Carlo simulation

Diffusion

Irradiation effect

Segregation

### ABSTRACT

Radiation induced segregation in ferritic Fe–Cr alloys is studied by Atomistic Kinetic Monte Carlo simulations that include diffusion of chemical species by vacancy and interstitial migration, recombination, and elimination at sinks. The parameters of the diffusion model are fitted to DFT calculations. Transport coefficients that control the coupling between diffusion of defects and chemical species are measured in dilute and concentrated alloys. Radiation induced segregation near grain boundaries is directly simulated with this model. We find that the diffusion of vacancies toward sinks leads to a Cr depletion. Meanwhile, the diffusion of self-interstitials causes an enrichment of Cr in the vicinity of sinks. For concentrations lower than 15%Cr, we predict that sinks will be enriched with Cr for temperatures lower than a threshold. When the temperature is above this threshold value, the sinks will be depleted in Cr. These results are compared to previous experimental studies and models. Cases of radiation induced precipitation and radiation accelerated precipitation are considered.

© 2015 Acta Materialia Inc. Published by Elsevier Ltd. All rights reserved.

## 1. Introduction

Ferritic Fe–Cr steels are good candidates as structural materials for the next generation of nuclear power plants (generation IV and fusion reactors) [1,2]. The addition of Cr prevents corrosion and the Fe–Cr ferritic form is weakly sensitive to the swelling phenomenon. However, the irradiation flux induces an increase of point defect concentrations – vacancies and self-interstitial atoms (I) – that migrate toward sinks where they are eliminated. These defect fluxes may induce a variation in the alloy composition in the vicinity of sinks called Radiation Induced Segregation (RIS) [3]. If this causes a Cr depletion, the alloy can become sensitive to corrosion. On the other hand, if this leads to a Cr enrichment, the local concentration can reach the solubility limit, causing Radiation Induced Precipitation (RIP), which could lead to embrittlement. RIS has been extensively studied in austenitic steels where Cr depletion and Ni enrichment are frequently observed at sinks. These tendencies are relatively well-understood, even if the interstitial contribution is still under discussion [3]. In ferritic steels, the situation is far from being clear: approximately 15 experiments have been reviewed by

Lu et al. [4] in very different materials and conditions, showing both depletions and enrichments in the vicinity of sinks. However, it is difficult to draw clear conclusions on how irradiation conditions and materials properties control the tendency towards enrichment or depletion. A systematic study, focusing on industrial steels with Cr content between 8 and 12% has been performed by Was et al. [5]. They observed that for given irradiation conditions, sinks tend to be enriched in Cr at low temperature and to be depleted in Cr at high temperature. Moreover, the Cr enrichment tends to decrease with the alloy Cr content. These tendencies are reproduced with the inverse Kirkendall model of Wharry et al. [6] and are attributed to a positive coupling of Cr with self-interstitials (dominant at low temperatures) and a negative coupling with vacancies (dominant at high temperatures). Other factors, such as grain boundary misorientation [7], interactions with C or other impurities [7,8] may influence the segregation of Cr at sinks.

In the present study, we limit ourselves to the Fe–Cr binary system in order to understand basic mechanisms controlling RIS at the atomic scale. Thermodynamics of Irreversible Processes (TIP) shows that a complete description of RIS requires a full determination of the Onsager coefficients  $L_{ij}$ , or alternatively, of partial diffusion coefficients  $d_{ij}$  [3]. Such a consistent description remains to be established for concentrated Fe–Cr alloys. Existing models are based on Density Functional Theory (DFT) calculations and multi-

\* Corresponding author.

E-mail address: [oriane.senninger@northwestern.edu](mailto:oriane.senninger@northwestern.edu) (O. Senninger).

frequency models that are only valid in the dilute limit [9,10], or have been extended to concentrated alloys using additional approximations [9,5,6]. Others use Molecular Dynamics (MD) simulations that rely on empirical potentials and only determine the self-interstitial contribution [11,12].

We present here a multiscale approach of RIS, starting from DFT calculations of the point defect migration energies. A diffusion model describing the variation of point defect properties with local composition is developed. Atomistic Kinetic Monte Carlo (AKMC) simulations are performed in order to (i) determine the  $L_{ij}$  coefficients and predict the RIS tendencies; and (ii) model the evolution of point defect and Cr concentration profiles under irradiation in the vicinity of a grain boundary (GB). AKMC simulations include the effect of non-homogeneous concentration fields and account for the stochastic nature of point defect migration. It also enables the simulation of RIP, when the RIS leads to a strong enrichment of Cr near GBs and therefore to nucleation of  $\alpha'$  precipitates.

In Section 2 we present a reminder of RIS principles in the framework of TIP. In Section 3, the diffusion model and the AKMC method are introduced. The fitting of parameters to DFT calculations is detailed and relevant point defects properties are discussed. In Section 4, the point defect tracer diffusion coefficients and Onsager coefficients are analyzed. The effect of composition and temperature on these Onsager coefficients is studied. Simulations of RIS and RIP near grain boundaries are also shown. We discuss these results by comparing them to previous models and experiments. We conclude by commenting on the limitations of our model, possible improvements and perspectives.

## 2. Thermodynamics of irreversible processes and radiation induced segregation

RIS is due to fluxes of vacancies ( $J_V$ ) and self-interstitials ( $J_i$ ) towards point defect sinks that, in an A-B alloy, induce fluxes of chemical species ( $J_A$  and  $J_B$ ). TIP describes the fluxes  $J$  as linear combinations of thermodynamic driving forces, i.e. chemical potential gradients [3]:

$$J_\alpha = -\sum_\beta L_{\alpha\beta} X_\beta \quad (1)$$

with  $X_\beta = \nabla \mu_\beta / (k_B T)$ .  $L_{\alpha\beta}$  are the Onsager coefficients,  $\mu_\beta$  the chemical potentials,  $k_B$  the Boltzmann constant and  $T$  the temperature.

In steady state, under the conditions where there is no precipitation and  $L_{\alpha\beta}$  coefficients are independent of the local composition, the gradient of B and V near a sink are related by:

$$\nabla C_B = -\frac{L_{AI} L_{AV}}{C_V (L_{AI} D_B + L_{BI} D_A)} \left( \frac{L_{BV}}{L_{AV}} - \frac{L_{BI}}{L_{AI}} \right) \nabla C_V \quad (2)$$

where  $D_A$  and  $D_B$  are intrinsic diffusion coefficients. This profile may also be expressed in term of partial diffusion coefficients:  $d_{\alpha V} = L_{\alpha V} / C_\alpha C_V$  and  $d_{\alpha I} = L_{\alpha I} / C_\alpha C_I$  [13,14].

The sign of the  $L_{\alpha\beta}$  coefficients corresponds to the direction of couplings. For example, in the A-B alloy if  $L_{BV} > 0$  fluxes of B and V are in the same direction and if  $L_{BV} < 0$  they are in opposite directions. In simple cases, general rules of concentration variations can be derived from point defect diffusion coefficients. RIS is thus often analyzed in terms of Inverse Kirkendall effect: for the vacancies, if B is the fast diffusing species (ie  $D_B > D_A$ ), a depletion of B at sinks is expected (note that it is only true when  $L_{BV} < 0$ ); for interstitials, if B is the fast diffusion species, an enrichment of B is expected ( $L_{BI}$  is always positive) [3]. On the other hand, in the case of significant attraction between solute atoms and vacancies,  $L_{BV}$  may be positive, leading to solute atoms dragged by vacancies and a

solute enrichment at sinks (this is called the drag effect). Beyond such interpretations, one must know the full set of  $L_{ij}$  coefficients in Eq. (2) and how they depend on temperature and concentration in order to determine the RIS profiles.

The  $L_{ij}$  coefficients are very difficult to extract from diffusion experiments but they can be in principle easily deduced from atomic scale simulations. This requires: (i) a good description of jump frequencies and their variation with respect to the local environment and (ii) a good method to compute the  $L_{ij}$  coefficients from the jump frequencies. For the second point, two strategies are possible:

1. A numerical determination of the  $L_{ij}$  (or  $d_{ij}$ ) coefficients by MD or AKMC simulations. MD simulations with an empirical potential have been used by Terentyev, Pechenkin et al. [11,12] for the coefficients of self-interstitials. Here we use AKMC simulations to directly measure the  $L_{ij}$  coefficients of both vacancies and self-interstitials.
2. An analytical calculation of the  $L_{ij}$  coefficients (or alternatively, of the partial diffusion coefficients) from point defects jump frequencies, using multi-frequency diffusion models valid for dilute systems. This approach has been applied to Fe–Cr alloys by Choudhury et al. [9] and by Was, Wharry et al. [5,6]. Those diffusion models were limited to short-range interacting alloys and the contribution to the  $L_{ij}$  coefficients of some vacancy jumps beyond the first nearest neighbor sites of the solute atom had to be neglected. Recently, long-range interaction models of the  $L_{ij}$  coefficients have been developed [15,16]). In concentrated alloys, due to the high complexity, approximate mean field methods are used to determine the  $L_{ij}$  coefficients [3].

## 3. Diffusion model and AKMC simulations

### 3.1. Diffusion model and effective pair interactions

The calculation of point defects jump frequencies is based on a rigid lattice model using effective pair interactions hereafter referred to as the “AKMC model”. We start from a previous version [17] that only includes vacancy diffusion. It assumes that the free enthalpy of a given atomic configuration can be written as a sum of effective pair interactions on a rigid bcc lattice.

Such “broken bond” models with constant pair interactions are widely used in AKMC simulations to model diffusive phase transformations in alloys [18–21]. However, Fe–Cr alloys have a special thermodynamic behavior, with strong vibrational and magnetic contributions. The latter are especially important: they lead to a change in the sign of the alloy mixing energy around 10 at.% Cr. In Ref. [17], magnetic and vibrational contributions are taken into account by introducing a temperature dependence on all interactions and by making Fe–Cr interactions on lattice sites dependent on local concentration (see Refs. [22,17]). This model generates solubility limits in good agreement with recently updated Fe–Cr phase diagrams [23,24], showing an asymmetrical miscibility gap (see Fig. 1 in Ref. [17]). It gives diffusion coefficients and kinetics of precipitation in good agreement with experimental data, in the range of temperatures and compositions considered here (300–950 K and up to 20% of Cr).<sup>1</sup>

<sup>1</sup> In Fe–Cr solid solutions, the ferro-to-paramagnetic transition leads to an increase of the diffusion coefficients that can be modeled by a correction of the vacancy migration barriers [17]. It is shown to significantly accelerate the precipitation kinetics in alloys with high Cr contents (above typically 25%). As we limit our study to concentrations lower than ~15%, such effects are not included in the present model.

Download English Version:

<https://daneshyari.com/en/article/7879175>

Download Persian Version:

<https://daneshyari.com/article/7879175>

[Daneshyari.com](https://daneshyari.com)