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Grain boundary segregation in low Cr Fe–Cr alloys: The effect of radiation induced vacancies studied by metropolis Monte Carlo simulations

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ABSTRACT

Radiation damage may modify the segregation state and phase separation conditions in Fe–Cr alloys with compositions and temperatures of technological interest. We use Metropolis Monte Carlo simulations to study segregation effects at the best stable variant of the $\Sigma = 5$ (2 1 0) grain boundary, in the 5–10 at.% range of Cr composition. The role of irradiation induced vacancies in segregation is discussed. At a low Cr composition, an oscillatory Cr segregation profile is evidenced in the vicinity of the boundary. Under specific conditions, Cr ordering is observed close to the boundary. The correlations between such ordering and local stress is discussed. The binding energy of vacancies to specific sites of the grain boundary is found to be positive and the interplay between Cr segregation and the clustering of vacancies at the boundary is discussed.

1. Introduction

Fe–Cr alloys represent a class of complex materials and many of their properties are not quite well understood. The interest in these alloys is connected to the fact that high-chromium ferritic/martensitic steels with bcc structure display high resistance to irradiation induced effects [1–4]. Therefore, they are the most promising candidate among structural materials to be utilized for advanced fission and fusion reactors [5]. The range of compositions of technological interest is around 9 to 12 percent chromium. In this range, a change of sign of mixing enthalpy versus composition takes place [6], attributed to frustration effects between ferromagnetic iron and antiferromagnetic Cr. This fact appears to have consequences for several properties of Fe–Cr alloys such as segregation at surfaces, interfaces and microstructural defects, mechanical properties or swelling under radiation [7–13]. A significant effort is undertaken nowadays in order to develop reliable models, as much as possible in synergy with experiments. Such efforts are discussed in several recent reviews [6,7] and represent the framework of this article. In our previous work, surface and grain boundary energetic and segregation were studied *ab initio* [14–17] as well as using equilibrium Monte Carlo techniques with semi-empirical potentials [17,18]. In this way, Cr depletion at surfaces was predicted *ab initio* and confirmed by Metropolis Monte Carlo (MMC) simulations in the whole range of technologically relevant compositions (5 to 20 percent Cr) and in a temperature range from 0 to 900 K, within which an order–disorder transition may occur. On the contrary, a Cr enrichment was observed at edge dislocations and dislocation loops while no significant effect was found at screw dislocations, suggesting the role of local stress.

Acknowledging the importance of local atomic configurations in equilibrium segregation, the present work focuses on equilibrium segregation at grain boundaries (GB) and at the surface of small voids which might result from irradiation, as well as on the interplay between vacancy clustering and Cr segregation at GBs. The symmetrical $\Sigma = 5$ (2 1 0) [0 0 1] boundary is selected as a case study. This GB allows for a number of different local atomic configurations according to local minima in the energy landscape associated with different translation vectors between two adjacent grains. A detailed discussion of these configurations will be provided in [19]. For the purpose of the present study, the most stable one is selected.

The simulation technique is briefly sketched in Section 2, the simulation results are provided in Section 3, starting with GB

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segregation and then discussing the role of vacancies in segregation. A short summary is given in Section 4.

2. Simulation technique

Metropolis Monte-Carlo (MMC) sampling was used within the isobaric-isothermal (*NPT*) statistical ensemble where the number of particles *N*, the pressure *P* and the temperature *T* are kept constant [18,20,21]. The method includes three types of trials: (i) Random displacement of all atoms from their current positions (by this trial, lattice relaxation and vibrational entropy are accounted for); (ii) Swapping of atoms of different kinds located at different lattice sites, selected at random (by this trial, the risk of trapping of the system in a local free energy minimum is limited); (iii) Overall volume change of the simulation box (by this trial, zero pressure is maintained constant, even in the case of structural transition). The decision on acceptance of a new configuration is based on the probability distributions presented in [20]. In what follows, one set of trials (i) and (ii) is termed a "macrostep".

The final configurations reported here correspond to averaging the atomic positions over the last $(1.5–2) \times 10^6$ macrosteps, once steady-state was reached (typically after a few millions of macrosteps). Steady-state was estimated as reached once the total energy of the system, the short-range order parameter and the size of the system have converged.

In order to optimize the convergence of the MMC, a quenching MD scheme is used first, in order to relax the atomic configuration from geometrical positions in the vicinity of the GBs. MD was also used to obtain configurations at constant volume and non-zero temperature. It was also employed to estimate the mean pressure on each atom from the force field.

In both MMC and MD simulations, the so-called two-band interatomic potential [22,23] is used, which expands the Ackland's second-moment expression [24] for the total energy of binary alloys with contributions from s-band electrons. Two versions of the potential were considered. The just recently developed one (Bonny [23]) is an improvement of the first (Olsson et al. [22]) that the calculated Fe–Cr phase diagram better complies with the experimental one in Cr-rich region. Differences in the Fe-rich region are very minor and were found of no significant influence on the results presented below. They were obtained with the Bonny's potential, except for few results found with the Olsson's potential, which will be explicitly mentioned in the text. Both potentials were developed so as to fit the properties of ferromagnetic Fe–Cr alloys, including the mixing enthalpy (as a function of the Cr concentration), and the mixed dumbbell energy. Although, the model does not treat magnetism explicitly, i.e. spins are not included; magnetic effects are accounted for indirectly, in an empirical way.

In all MMC studies the initial spatial distribution of Cr and of vacancies when they are considered was selected at random in the rectangular model box according to a uniform distribution. The side lengths of boxes were equal to ~15 lattice units or longer. This was found sufficient to capture main bulk precipitation features [21], and the properties of the GB and of its image generated by the periodic boundary conditions.

Applying the same algorithm to a bulk system with the same potential already allowed to clearly distinguish between a solid solution state (labelled ss in what follows), with a tendency to order (negative short-range order parameter), and a phase where FeCr precipitates are formed (labelled pp in what follows) [21]. In particular, regarding the compositions considered here, the transition between pp and ss was found to occur around 600 K in $Fe_{90}Cr_{10}$, consistently with experiment and recent thermodynamic studies [25,26]. Instead, pp never occurred in $Fe_{95}Cr_5$, irrespective of temperature and a tendency to order is found in ss, also in agreement with experiments and thermodynamic studies mentioned.

3. Results and discussion

3.1. Grain boundary segregation

The selected $\Sigma = 5$ (2 1 0) [0 0 1] GB is characterized by a (2 1 0) boundary plane and a [0 0 1] tilt axis. The tilt angle is such that both halves of the bi-crystal have a coincidence site lattice with five sites in its motif. Pairs of GBs with a coincidence site lattice are conveniently generated using Born von Karman periodic boundary conditions. Such boundaries are frequently observed because they correspond to relative minima in the tilt angle dependence of the GB excess free energy. The simplest GB in the cubic structures is a stable $\Sigma = 3$ one, characterized by the lowest excess energy and the lowest disorder. The $\Sigma = 5$ case represents a compromise between the lowest Σ value, requiring the smallest simulation box, and boundaries displaying no periodicity commensurate with the cubic structure. This does not determine the atomic configuration at the GB uniquely. We identified five possible metastable configurations generated by different shifts of one grain with respect to the other, parallel to the GB plane. The best stable one was selected to be studied here. After each atomic position is

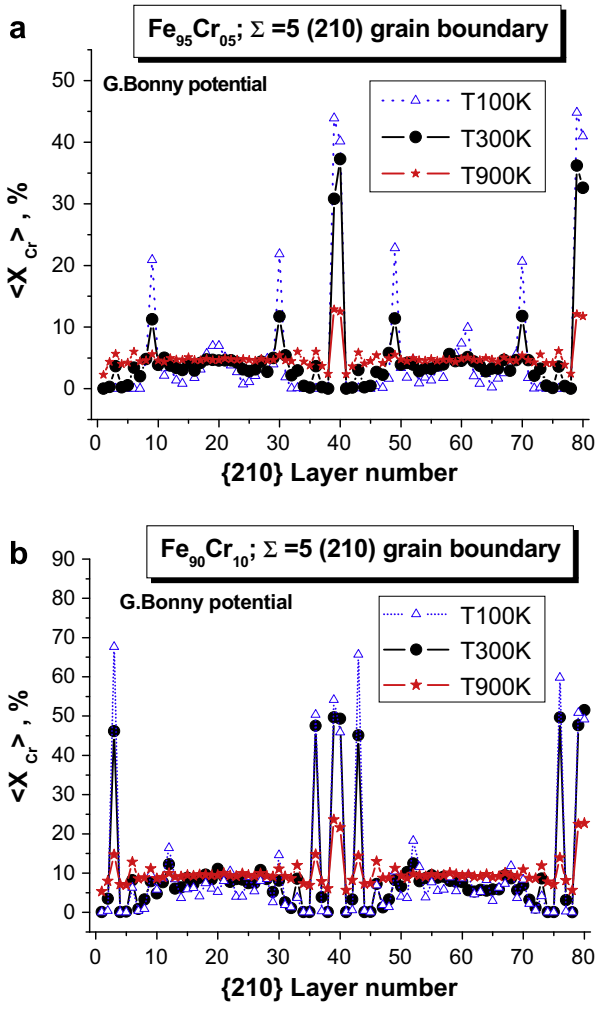

Fig. 1. Average concentration of Cr atoms in each layer (layer 40 is the $\Sigma = 5$ (2 1 0) GB plane in the middle of the model box) in an $Fe_{95}Cr_5$ (a) and in $Fe_{90}Cr_{10}$ (b) at different temperatures.