Segregation and Precipitation in iron-chromium alloys: thermal ageing and irradiation effects

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Abstract

We present a brief review of recent advances in the atomistic modeling of segregation and precipitation kinetics in iron-chromium alloys, during thermal ageing and under irradiation. The approach takes into account the real diffusion mechanisms: vacancy and, under irradiation, self-interstitial jumps. Migration barriers are computed with effective pair interactions fitted on ab initio calculations. The simulations show how point defect properties control long term kinetic behaviors. The role of magnetic properties is especially emphasized.

Introduction

Iron-chromium alloys are the basis for ferritic and ferritic-martensitic steels that will be used in future fission (generation IV) and fusion nuclear reactors. With Cr content between typically 8 to 12% [1], or even 14% in the matrix of some oxide dispersion-strengthened steels [2], one can expect the precipitation of a Cr-rich α’ phase (Fig. 1) that can be strongly accelerated under irradiation, due to point defect supersaturation. This precipitation can cause hardening and embrittlement.

Radiation-induced segregation (RIS) is another important technological problem. It can lead to a Cr depletion at grain boundaries and therefore to a loss of corrosion resistance and again, to embrittlement. RIS in austenitic steels is well known and presents almost systematic trends: depletions of Cr and enrichments of Ni at grain boundaries. In ferritic steels, the experimental situation is far from being so clear: depletions and enrichments of Cr have been observed, without clear correlation with the irradiation conditions and the materials properties [4]. Segregation and precipitation occur by formation, migration and elimination of point defects (vacancies and self-interstitials). In the following we present a model that includes these mechanisms, and combines ab initio and atomistic kinetic Monte Carlo (AKMC) simulations. We address problems by order of complexity: first isothermal precipitation (thermal ageing), then precipitation accelerated by irradiation and finally radiation-induced segregation. In each case we will try to emphasize the link between point defect properties and the evolution of microstructure.

Interaction and Diffusion Model

At the atomic scale, Fe and Cr atoms migrate by exchanges with vacancies and self-interstitials. The latter are only present under irradiation, due to their higher formation energies. Point defect diffusion properties are mainly determined by their Gibbs free energies of migration (or migration barriers), and by the way they depend on the local atomic environment [5]. In the AKMC simulations, we assume that the Gibbs free energy of an atomic configuration (i.e. a given distribution of Fe and Cr atoms and point defects, on the crystal lattice) is a sum of effective pair interactions between i and j species [6,7]. The pair interactions include energetic and entropic contributions, the latter mainly of vibrational and magnetic origin. The migration barriers are then computed using a “broken-bond” approach, i.e. by counting the pairs that are broken around the original positions and formed around the saddle-point positions, for each possible point defect jump. The pair interactions are fitted on ab initio calculations of atomic distribution mixing energies and point defects migration barriers [6,7].

Fe-Cr alloys have original magnetic properties that affect their thermodynamic and kinetic behavior, and must therefore be taken into account in the diffusion model. Ab initio calculations show in particular that the mixing of Fe and Cr atoms induces magnetic frustrations, due to competing ferro- and antiferro-magnetic tendencies [8,9]. This leads to short-range ordering in under-saturated Fe-Cr alloys [10] and explains the asymmetry in the α-α’ miscibility gap (Fig.1). To reproduce this feature, pair interactions depend on the local composition [11].

Entropic vibrational and magnetic contributions are both important in Fe-Cr alloys, and are taken into account by a temperature dependence of the pair interactions [6,7,11].

Isothermal precipitation kinetics

Without irradiation, the only operating diffusion mechanism is vacancy jump. The tracer and interdiffusion
diffusion coefficients of the Monte Carlo model can be compared to available experimental data [7]. Thanks to a good description of thermodynamics and diffusion properties, the precipitation kinetics of Monte Carlo simulations [6,7] are in good agreement with experimental studies using tomographic atom probe measurements [12] or small-angle neutron scattering [13,14], in a large range of compositions where precipitation occur by nucleation-growth as well as by spinodal decomposition.

**Figure 2.** Tracer diffusion coefficients of Fe and Cr in iron. The dots correspond to experimental, the lines to the Monte Carlo model [7].

In iron based alloys, a key point is the effect of the ferro-to-paramagnetic transition. It produces an acceleration of diffusion at temperatures just below the Curie point (770°C), leading to a strong curvature of the Arrhenius diffusion diagrams (fig. 2).

**Figure 3.** Time evolution of the peak position of the structure factor, during the α-α’ decomposition of Fe–Cr alloys of different compositions, at different temperatures. Open squares: small angle neutron scattering measurements [13,14]; circles: AKMC simulations, not taking into account the acceleration of diffusion at the ferro-to-paramagnetic transition; triangles: AKMC simulations, taking into account the acceleration of the diffusion [7]. This acceleration is taken into account in the Monte Carlo simulations. In concentrated alloys (typically more than 30%Cr), the precipitation kinetics is strongly accelerated at even lower temperatures (500-540°C), because of the rapid decrease of the Curie temperature with the Cr content (fig. 1). This is illustrated in figure 3 that show the evolution of the position of the diffusion peak at small angles during α-α’ decomposition, as observed in small-angle neutron scattering experiments and as predicted by the Monte Carlo simulations. Nanoscale 1D interdiffusion experiments are underway in Fe-Cr multilayers and can also be directly compared to Monte Carlo simulations [15].

**Acceleration of precipitation under irradiation**

It is well-known that ion, neutron or electron irradiations sustain point defect concentrations far above the equilibrium values, leading to radiation enhanced diffusion and to the acceleration of diffusive phase transformations [16]. Monte Carlo simulations can be used to quantify the acceleration, depending on irradiation conditions. In Fe-18%Cr for example, during an isothermal annealing at 290°C, Monte Carlo simulations predict a very slow α’ precipitation (Fig. 4): the maximum density of precipitates is reached after more than 10^{10} sec (approximately 300 years).

**Figure 4.** Evolution of the density d_p and radius R of α’ precipitates in Fe-18%Cr, during a thermal ageing at 290°C, and under an irradiation at 3.4×10^{-7} dpa.s^{-1} and the same temperature. The lines correspond to the Monte Carlo simulations, the circles to tomographic atom probe observations in a ferritic steel of similar composition, after neutron irradiation at the same flux (Bachhav et al. [13]). Irradiation at a dose rate of 3.4×10^{-7} dpa.s^{-1} accelerates the precipitation by 6-7 orders of magnitudes. Under irradiation, point defect concentrations depend on the density of sinks (grain boundaries, dislocations, etc.). AKMC simulations are performed with a constant sink density – typically one grain boundary in the middle of the simulation box. To get a more precise estimation of the evolution of sink densities and point defect concentrations, cluster dynamics [17] have been used: the physical time scales of the Monte Carlo simulations is rescaled accordingly and one gets precipitation kinetics in good agreement with the few available experimental results (Fig. 4).

Some experimental observations are still difficult to understand: for example it seems that α’ precipitation is
observed during neutron irradiations [13,14], but not under ion irradiations [15]. Monte Carlo simulations must be developed to test other possible effects: the one of ballistic mixing that occur in displacement cascades, or the one of carbon and other impurities (O,N), which are known to strongly interact with the vacancies.

**Radiation Induced Segregation (RIS)**

This phenomena results from the elimination of excess point defects on sinks such as dislocations, grain boundaries, or free surfaces. Permanent fluxes of point defects towards the sinks are then sustained, i.e. permanent fluxes of chemical species. Very often, this leads to a modification of the local composition near the sinks. RIS must not be confused with the usual equilibrium segregation: it can enhance or reduce it, and it must vanish when irradiation is stopped. Theoretically, RIS can be analyzed properly in the framework of the thermodynamics of irreversible processes, that gives the fluxes of a specie $\alpha$ (atom or defect) as a function of the gradients of chemical potentials, $\nabla \mu_\beta$:

$$J_\alpha = - \sum_{\beta} L_{\alpha\beta} k_B T \nabla \mu_\beta$$

where $k_B$ is the Boltzmann constant and $T$ the temperature. The tendencies to solute enrichment or depletion near the sinks are controlled by the Onsager coefficients, $L_{\alpha\beta}$. In Fe-Cr alloys, the steady-state gradient of Cr is proportional to the steady-state gradient of vacancies, according to [21]:

$$\nabla C_{Cr} = \frac{L_{FeV} L_{FeI}}{C_v (L_{FeI} D_{Cr} + L_{CrI} D_{Fe})} \left( \frac{L_{CrI}}{L_{FeV}} \frac{L_{CrI}}{L_{FeI}} \right) \nabla C_V$$

One must observe an depletion of Cr near the sinks if $L_{CrI}/L_{FeV} > L_{CrI}/L_{FeI}$, an enrichment of Cr in the opposite case. Onsager coefficients can be directly estimated in Monte Carlo simulations, from the displacements $\Delta R$ of the corresponding species during a time $t$:

$$L_{\alpha\beta} = \frac{1}{6Vk_B T} \langle \Delta R_\alpha \Delta R_\beta \rangle$$

In binary alloys with less than 15% of Cr [22], simulations show that one should observe enrichments of Cr near point defect sinks at low temperatures, and depletions at high temperatures (Fig. 5). This behavior is readily explained by point defect properties in pure $\alpha$-iron. Ab initio calculations show that the interaction between Cr atoms and vacancies in iron is weak, and that the migration barrier of the Cr-V exchange is smaller than the barriers of the Fe-V exchanges [6]: this explains why the diffusion of Cr is more rapid than the diffusion of Fe (Fig. 2) and this also means that fluxes of Cr and fluxes of vacancies are always in opposite directions. In such circumstances, the elimination of vacancies at sinks always tends to drive a depletion of Cr. Precise self-consistent mean-field diffusion models [23], recently developed in the dilute limit, are in good agreement with this prediction and show that Cr has an atypical behavior, by comparison with other substitutional impurities in iron. In most other cases, stronger attractive interactions between impurities and vacancies lead to a “drag-effect” at low temperatures – the migration without dissociation of solute-vacancy complexes – and therefore tend to drive an enrichment of solute at sinks.

Ab initio calculations of interstitial properties also show that in pure iron alloys, the (110) mixed Fe-Cr dumbbell is stable and has a smaller migration barrier than the other self-interstitial configurations [22]: as for the vacancies, this leads to a preferential diffusion of Cr by the interstitial mechanism, but this time Cr and interstitial diffuse in the same direction, producing a Cr enrichment at the sinks. Monte Carlo simulations predict that these tendencies remain true in solid solution with Cr concentration up to at least 15%.

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**Figure 5. Evolution of the ratios of Onsager coefficients $L_{CrI}/L_{FeI}$ and $L_{CrV}/L_{FeV}$ with the temperature, for different alloy compositions, measured by Monte Carlo simulations.**

Simulations have been also performed to model directly the evolution of point defects and solute distributions near a grain boundary. This enables to study the interaction between segregation and precipitation [22]. Figure 6 gives a simple example (without precipitation) of simulated concentration profiles, during the irradiation of a Fe-10%Cr alloy at 650 K. As expected from the analysis of the Onsager coefficients (Fig. 5), at this temperature the interstitial contribution dominates and one observes an enrichment of Cr. On the contrary at 950K (not shown here) vacancy contribution is dominant and Cr depletion occur [22].

A similar behavior has been experimentally observed in some ferritic steels [24], but is far from being systematic [4]. Simulations results nevertheless help to understand the origin of the variety in experimental observations. In
ferritic steels, according to the simulations, RIS is controlled by a balance between the contributions of vacancies and interstitials. In binary alloys, it is predicted that the former dominates at high temperatures, the latter at low temperatures. But both contributions are very close, especially above 600K (fig. 5) and small perturbations may easily reverse the balance. Monte Carlo simulations and Self-consistent mean field models [23] show indeed that small differences in the migration barriers, of the order of 0.1eV or even less, can sufficiently affect the Onsager coefficients to reverse the segregation tendency. Such perturbations could come from magnetic and vibrational contributions (only summarily described in the present diffusion model), from stresses, from impurities (carbon, etc.). By contrast RIS in austenitic steels is not controlled by such a subtle balance. The elimination of vacancies tends to produce a depletion of Cr and an enrichment of Ni while, according to different studies, the elimination of interstitials has either the same [24] or negligible effect [16].

**Figure 6. Monte Carlo simulation of radiation induced segregation of Cr near a grain boundary. Top: steady-state concentration profiles of point defects, Bottom: concentration profiles of Cr at two successive doses.**

**Conclusion**

Atomic modeling of point defect diffusion mechanisms, combining ab initio calculations and kinetic Monte Carlo simulations, has provided a better understanding of ageing of iron-chromium alloys during thermal annealing as well as under irradiation. Magnetism plays a key role in these alloys, affecting thermodynamic and diffusion properties. During thermal ageing, the Monte Carlo simulations – using a unique set of parameters and no fitting on the precipitation kinetics – are in good agreement with experimental results, both in nucleation-growth and spinodal decomposition regimes. In alloys with more than 30%Cr, the ferro-to-paramagnetic transition strongly accelerates the precipitation kinetics. The effect is not significant for lower concentrations, considered for nuclear applications. Below 300°C the precipitation is much slower, but it can be accelerated by irradiation, due to point defect supersaturations. A simple model of binary Fe-Cr alloy gives a reasonable agreement with available experimental data, but further studies are required to assess possible effects of impurities or ballistic mixing. The modelling of radiation-induced segregation is especially challenging, due the close competition between vacancies and interstitials, a fact that may also explain the variety of experimental observations.

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