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# Radiation-accelerated precipitation in Fe–Cr alloys

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ABSTRACT

The kinetics of phase separation in Fe–Cr alloys under irradiation is modeled by Atomistic kinetic Monte Carlo simulations that include the formation, migration and elimination of vacancies and self-interstitials at point defects sinks. The evolution of the sink density is modeled by cluster dynamics, and taken into account in the Monte Carlo simulations by a rescaling of the time. The results are in good agreement with available experimental observations of neutron irradiation at 290 °C. The irradiation is found to accelerate the kinetics of phase separation by orders of magnitude, with an acceleration factor given by the increase in point defect concentrations. The microstructure evolution is qualitatively the same as during isothermal annealing, except in the vicinity of point defect sinks. The effects of equilibrium and radiation induced segregations at grain boundaries are considered. The ballistic mixing occurring in displacement cascades is modeled, and is found to be insufficient to produce the dissolution of chromium rich precipitates at 290 °C, even at high dose rates. Therefore, it cannot explain the absence of precipitation observed during ion irradiations.



## 1. Introduction

Iron-chromium alloys are the model system of ferritic and ferritic-martensitic steels that will be used in future fission (generation IV) and fusion nuclear reactors. Below approximately 600 °C (Fig. 1), Fe–Cr solid solutions undergo a coherent phase separation between an iron rich phase ($\alpha$) and a chromium rich phase ($\alpha'$), with body centered cubic (bcc) lattices and very close lattice parameters. This decomposition is the origin of the "475 °C Embrittlement", a phenomenon known since the thirties and that has been related to the $\alpha'$ precipitation in 1953 [1].

Kinetics of isothermal precipitation in Fe–Cr alloys have been extensively studied by small-angle neutron scattering (SANS) [3,4], Mössbauer Spectroscopy [5–7], field ion microscopy and 3D atom probe (3DAP) [8–13]. Most of these studies deal with relatively highly concentrated alloys at temperatures of 450 °C or above, where precipitation kinetics is rapid enough. At lower temperatures $\alpha'$ precipitation becomes slower, even in highly supersaturated alloys: for example, it is not observed in a Fe-32%Cr alloys after an isothermal annealing of 2150 h at 290 °C [14]. As usual, because of slow kinetics the low temperature region of the phase diagram is mainly known from extrapolation from higher temperatures, leading to some controversies [2,15]. But for nuclear applications with Cr concentrations between 8 and 12% [16], or even 14% for the matrix of some oxide dispersion-strengthened steels [17], one may expect a $\alpha'$ precipitation: according to the most recent phase diagrams (Fig. 1), at $T < 300$ °C for 9% of Cr, at $T < 450$ °C for 14% of Cr. The precipitation may be too slow to be observed during isothermal annealing on accessible times, but it can be strongly accelerated by irradiation, because point defect concentrations may then be higher than the equilibrium ones (by orders of magnitude), leading to much faster diffusion. Indeed, $\alpha'$ precipitation has been observed under neutron irradiations: at 290 °C in model alloys with 9–18% of Cr [18] and with 32% of Cr [14], at 300 °C in Fe-12%Cr [19,20] and Fe-12.5%Cr [21] alloys, at 325 °C in martensitic steels with 7 and 11% of Cr [22], at 300 and 450 °C in 10 and 16%Cr models alloys [23]. On the opposite, a recent study [24] has shown no $\alpha'$ precipitates in a Fe-12%Cr alloy irradiated by ions at 300 °C, while they were observed in the same alloy during neutron irradiation at the same temperature, with a lower dose rate ($7 \times 10^{-7}$ instead of $2 \times 10^{-4}$ dpa.s$^{-1}$). On the modeling side, cluster dynamics has been used to model the acceleration of Cr precipitation in Fe-12.5%Cr at 300 °C: the experimental kinetics were successfully reproduced by using the $\alpha/\alpha'$ interface energy as a fitting parameter [25].

Besides a strong acceleration, these experiments show few differences in the precipitate microstructure between isothermal agings and irradiations. One exception is the study of a Fe-32%Cr alloy irradiated by neutrons at 290 °C: isolated $\alpha'$ precipitates were observed [14], while alloys with such high Cr contents usually display bi-

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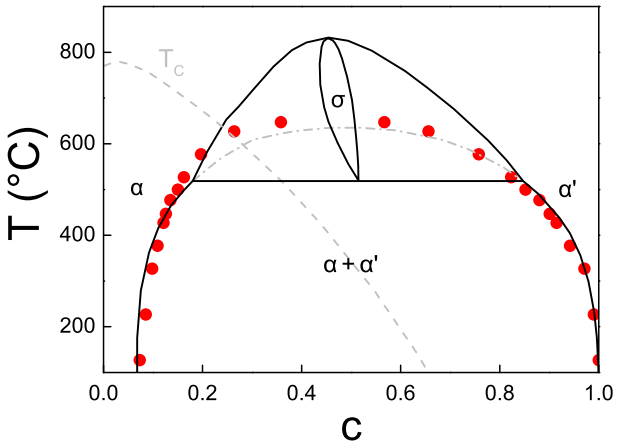


**Fig. 1.** The Fe–Cr Phase Diagram, from Ref. [2] (the circles show the miscibility gap of the AKMC model).

percolated microstructures when annealed without irradiation at higher temperatures. Moreover, the Cr solubility limit was found to be much higher under irradiation than at equilibrium (≃30%, instead of ≃9%). Both effects were attributed to the ballistic mixing occurring within displacement cascades [14]. These conclusions seem hardly compatible with the experiments of Mathon et al. [22], performed at a slightly higher temperature (325 °C), suggesting a much lower solubility, close to the equilibrium one. Another difference with isothermal annealing is the observation under irradiation of precipitate free zones (PFZ) in the vicinity of cavities [26], grain boundaries, or other incoherent precipitates (such as carbides or nitrides [27]). To our knowledge, this has not been observed for $\alpha'$ precipitation without irradiation.

The aim of the present study is to model the kinetics of $\alpha - \alpha'$ phase separation under irradiation and especially to quantify the acceleration due to the point defect supersaturation. We also consider possible effects that could qualitatively change the precipitation microstructure, such as those of ballistic mixing and of grain boundaries. We use Atomistic Kinetic Monte Carlo (AKMC) simulations that take into account the diffusion of Fe and Cr by vacancy and self-interstitials, including the formation, migration, mutual recombination and annihilation of these point defects at sinks. The parameters of the model have been fitted to ab initio calculations and it has been successfully applied to model kinetics of precipitation during isothermal annealing [28,29] and radiation induced segregation [30].

A key point to model the acceleration of precipitation is to deal with realistic point defects concentrations. Therefore in Section 2, we first recall some important aspects of radiation effects on point defect concentrations and diffusion, as revealed by homogeneous kinetic equations and cluster dynamics, emphasizing especially the role of dose rate and point defect sink densities. In Section 3 we present the AKMC simulations that are performed using different dose rates and different, but constant, sink densities. We explain how they can be improved to take into account a more detailed evolution of the sink densities, as given by cluster dynamics. The results of the simulations are presented in Section 4 and compared with experimental results.

## 2. Point defect concentrations and diffusion under irradiation

The diffusion coefficients of substitutional elements (in our case, Fe and Cr) are proportional to point defect concentrations. In a pure metal for example, if the contribution of di-vacancies, di-interstitials and other point defect clusters are negligible, the self-diffusion coefficient is given by:

$$D^* = f_i c_i D_i + f_v c_v D_v \tag{1}$$

where $D_i$ and $D_v$ are the diffusion coefficients of vacancies and self-interstitials, $f_i$ and $f_v$ some correlation factors (in pure metals, constants close to 1), $c_i$ and $c_v$ the point defect concentrations [31,32]. Under irradiation these concentrations may be much higher than the equilibrium values, $c_i^{eq}$ and $c_v^{eq}$. Several rate theory models have been proposed to estimate the evolution of $c_i$ and $c_v$. Most simple ones only consider mono-vacancies and mono-interstitials in a homogeneous system, with concentration evolutions given by:

$$\begin{aligned} \frac{dc_v}{dt} &= G - Rc_i c_v - \sum_s k_{sv}^2 D_v (c_v - c_{sv}) = G - Rc_i c_v - K_v (c_v - c_v^{eq}) \\ \frac{dc_i}{dt} &= G - Rc_i c_v - \sum_s k_{si}^2 D_i (c_i - c_{si}) = G - Rc_i c_v - K_i (c_i - c_i^{eq}) \end{aligned} \tag{2}$$

$G$ is the point defect production rate, or dose rate (in dpa.s$^{-1}$), $R = 4\pi r_c (D_i + D_v)/\Omega$ is the rate of recombination between vacancies and interstitials (where $\Omega$ is the atomic volume and $r_c$ the distance of spontaneous recombination). The third terms in Eq. (2) correspond to the elimination of point defects on the different sinks $s$ of the microstructures: grain boundaries, free surfaces, point defect clusters, etc. $c_{sv}$ and $c_{si}$ are the point defects concentrations at the sinks (where they remain at their equilibrium values, $c_{sv} = c_v^{eq}$ and $c_{si} = c_i^{eq}$). The sink strengths $k_{sv}^2$ and $k_{si}^2$ have been computed for common sinks [33]. For example, for a thin film geometry with planar sinks separated by a distance $L$, $k_s^2 \simeq 12/L^2$.

Usually $c_v \gg c_v^{eq}$ and $c_i \gg c_i^{eq}$, and the steady-state solutions of Eq. (2) are:

$$\begin{aligned} c_v^{st} &= -\frac{K_i}{2R} + \sqrt{\frac{K_i^2}{4R^2} + \frac{GK_i}{RK_v}} \\ c_i^{st} &= -\frac{K_v}{2R} + \sqrt{\frac{K_v^2}{4R^2} + \frac{GK_v}{RK_i}} \end{aligned} \tag{3}$$

Time evolutions are easily obtained by numerical integration of Eq. (2). Using Eq. (1), and considering that Eq. (2) imposes $c_i D_i \sim c_v D_v$ in the steady-state, diffusion under irradiation is accelerated by a ratio $2(c_v^{st}/c_v^{eq})$ after a short transient regime.

In simple cases the sink microstructure and the sink strength are supposed to be constant, but in general they evolve during the irradiation, although much more slowly than the point defect concentrations. The annihilation of point defects on pre-existing dislocations can produce a climb of the dislocation network, and point defects can form vacancy or interstitial clusters directly in displacements cascades or after subsequent evolution. Cluster dynamics (CD) methods, based on generalized rate theory equations, give the evolution of clusters of $j$ defects, according to:

$$\frac{dc_j}{dt} = G_j + \sum_k w(k,j) c_j - \sum_k w(j,k) c_j - L_j \tag{4}$$

where $G_j$ is the production rate of clusters of $j$ defects, $w(k,j)$ and $w(j,k)$ the rate of absorption or emission of a cluster of size $j$ by a cluster of size $k$, and $L_j$ gives the rate of elimination of the clusters on the sinks other than point defects clusters. In the following, we will use the CD code Crescendo [34], with the parameters