



Computational metallurgy and changes of scale / Métallurgie numérique et changements d'échelle Atomic simulations of diffusional phase transformations

Simulations atomiques des transformations de phases contrôlées par la diffusion

Emmanuel Clouet, Frédéric Soisson*

CEA Saclay, service de recherches de métallurgie physique, 91191 Gif-sur-Yvette, France

ARTICLE INFO

Article history:

Available online 17 August 2010

Keywords:

Precipitation

Nucleation

Kinetic Monte Carlo

Mots-clés :

Précipitation

Germination

Monte Carlo cinétique

ABSTRACT

We present recent applications of the atomistic diffusion model and of the kinetic Monte Carlo (AKMC) algorithm to alloys of industrial interest or to model systems. These applications include study of homogeneous and heterogeneous precipitation during thermal ageing as well as of phase transformation under irradiation. The AKMC simulations are also used to test the main assumptions and limitations of more simple models and classical theories used in the industry, e.g. the classical nucleation theory.

© 2010 Académie des sciences. Published by Elsevier Masson SAS. All rights reserved.

R É S U M É

Nous présentons des applications récentes d'un modèle de diffusion atomique et de simulations Monte Carlo cinétiques à des alliages d'intérêt industriel ainsi qu'à des systèmes modèles. Ces applications se concentrent sur l'étude de la précipitation homogène et hétérogène au cours de vieillissements thermiques, ainsi que sur les transformations de phase sous irradiation. Les simulations de Monte Carlo cinétique sont également employées pour valider les hypothèses et tester les limites des descriptions classiques des transformations de phase, comme la théorie classique de germination.

© 2010 Académie des sciences. Published by Elsevier Masson SAS. All rights reserved.

1. Introduction

Many theoretical approaches have been developed to model the decomposition kinetics in metallic solid solutions, in weakly supersaturated alloys where classical nucleation–growth–coarsening regimes are observed [1,2], as well as in highly supersaturated ones, where spinodal decomposition occurs [3]. The development of theoretical models is of high practical interest, but faces the fact that the kinetics of phase transformations are very sensitive to inevitable simplifying assumptions and to parameters which are difficult to precisely measure by experimental techniques.

An alternative approach is to start from an atomic modelling of the diffusion events that govern the phase transformation. Such approach has become more efficient thanks to: (i) the development of new atomistic kinetic Monte Carlo (AKMC) methods, which naturally take into account the key phenomena that control the kinetics pathways, especially the correlation effects of diffusion and the thermal fluctuations in the solid solutions; and (ii) the progress of *ab initio* calculations, especially since the generalisation of the Density functional theory (DFT), which provide a reliable way to compute the AKMC parameters. Since their early development, Monte Carlo simulations have proven to be a powerful tool in the field

* Corresponding author.

E-mail addresses: emmanuel.clouet@cea.fr (E. Clouet), frederic.soisson@cea.fr (F. Soisson).

of thermodynamics and dynamics of phase transformations. Some general reviews can be found in [4,5]. Here we focus on the kinetics of phase transformations in alloys, from the viewpoint of the physical metallurgist: special attention is paid to the evolution of the precipitation microstructure, to the transformation kinetic pathway (including its timescale) and to the underlying atomic diffusion mechanisms.

In the first part of this short review, we present a few recent AKMC simulations of diffusive phase transformations in model systems of industrial interest. We emphasise the effects of diffusion properties on the evolution of the precipitation microstructure. In most simple situations, the determination of key Monte Carlo parameters is reliable enough to provide a quantitative agreement with experimental results, at least for the beginning of the phase transformation. In the second part, we show that AKMC simulations are also useful to validate and improve simpler theoretical models and simulation methods which can then be used to reach longer ageing times.

2. Diffusion models and Monte Carlo algorithms

At the atomic scale, diffuse phase transformations are rather simple indeed. They result from the jumps of point defects, involving a small number of mechanisms: in substitutional alloys, vacancy jumps – by far the most common mechanism – or for small solute atoms such as C and N in iron, direct jumps between interstitial sites (see, e.g. Ref. [6]). These jumps i are thermally activated processes, and when the activation energies or migration barriers ΔE_i^{mig} are much larger than the thermal fluctuations $k_B T$, the corresponding frequencies are given by: $\Gamma_i = \nu_i \exp[-\Delta E_i^{\text{mig}}/(k_B T)]$, where ν_i is an attempt frequency.

2.1. Residence time algorithm

Once the diffusion mechanisms and jump frequencies Γ_i are known, Monte Carlo simulations can be used to generate a sequence of atomic configurations, according to the physical evolution of the system. A convenient class of MC algorithms are residence time, or continuous time algorithms [7,8]. At each Monte Carlo step, one transition is chosen with a probability proportional to the corresponding jump frequency, and the time is incremented by $t_{\text{MC}} = 1/\sum(\Gamma_i)$, where the sum runs over all the possible jumps at that step.

2.2. Diffusion models

The main difficulty of an atomistic modelling is to compute the jump frequencies and the way they depend on the atomic configuration. Nowadays, DFT calculations provide a reliable way to compute migration barriers for various environments, taking into account the atomic relaxations, at the initial and saddle-point positions. Unfortunately, these methods remain quite time consuming and the number of possible configurations, i.e. of migration barriers, increases very rapidly with the number of alloying element and the range of interactions. As a consequence, it seems impossible – in the foreseeable future – either to compute and tabulate all the possible migration barriers before the simulation, or to performed on-the-fly DFT calculations during the simulation. Empirical interatomic potentials can be used instead of *ab initio* methods, but this only shifts the problem, because, in principle, it should require a complete fitting procedure of the potential parameters on reliable DFT barriers for the various configurations.

A reasonable compromise is to use a much simpler energetic model, involving a few parameters fitted on the key thermodynamic quantities and migration barriers, deduced from experimental data and/or from *ab initio* calculations. Several “broken-bond models”, using pair interactions on rigid lattice approximations, have been proposed [9,10]. A natural choice is to write the activation energy as the difference between the binding energy of the jumping atom at the saddle point and the sums of all the bonds in the initial configuration that are destroyed by the jump. A restriction imposed by the rigid lattice approximation is that the precipitating phase and the parent phase need to be described on the same lattice. This limits AKMC simulations to the modeling of coherent phase transformations. Nucleating precipitates are usually coherent at the earliest stage of phase transformation, which therefore justifies the use of AKMC simulations, at least for the precipitation onset.

2.3. Point defect concentrations

Together with the point defect migration barriers and jump frequencies, the phase transformation kinetics depend on the point defect concentrations. For the usual case of diffusion by vacancy jumps, it can be assumed that a simulation performed with one vacancy in a system of N atoms gives the physical kinetics, if one applies a rescaling of the time according to:

$$t = t_{\text{MC}} \times C_V^{\text{MC}} / C_V^{\text{eq}}$$

where t_{MC} is given by the residence time algorithm, $C_V^{\text{MC}} = 1/N$ and C_V^{eq} being respectively the average vacancy concentration in the Monte Carlo simulation and the real equilibrium vacancy concentration. Such a rescaling is justified as long as the vacancy concentration is low enough (so that interactions between vacancies can be neglected) and the transformation is slow enough (so that the vacancy concentration remains at equilibrium).

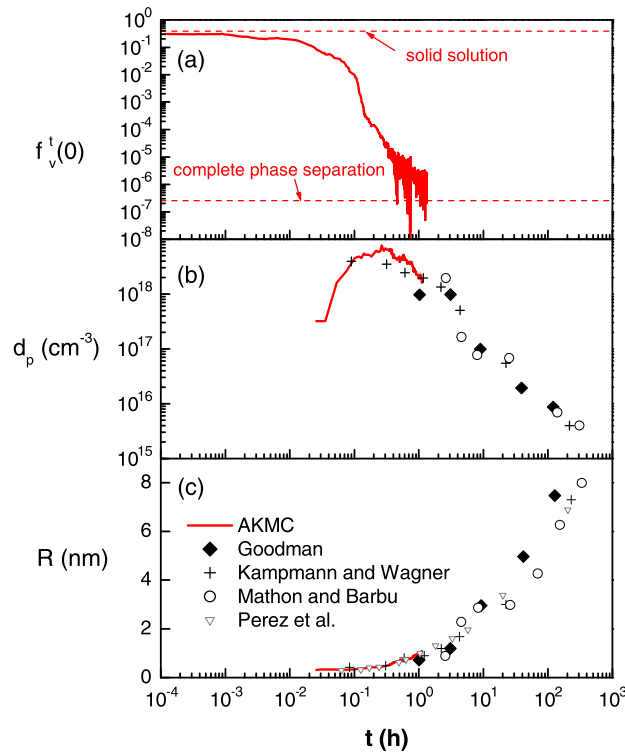


Fig. 1. Monte Carlo simulation [13] of the precipitation kinetics in Fe–1.34 at.% Cu during thermal ageing at 500 °C. Evolution of (a) the fraction of time spent by the vacancy in pure iron, (b) the density of precipitates, (c) the precipitate radius. The solid lines correspond to the simulations, the symbols correspond to experimental studies.

Fig. 1. Simulation Monte Carlo [13] d'une cinétique de précipitation dans un alliage Fe–1.34 at.% Cu au cours d'un vieillissement thermique à 500 °C. Évolution (a) de la fraction de temps passée par la lacune dans le fer pur, (b) de la densité de précipités, (c) du rayon des précipités. Les lignes continues correspondent aux simulations, les symboles aux études expérimentales.

It is worth noticing that in a system undergoing a phase transformation, C_V^{eq} can dramatically change when the vacancy formation energies in the various phases strongly differ. It is difficult to estimate directly, because it depends on the fractions of different phases, on their composition, on the fraction of the interfaces, etc. A simple way to get a physical time rescaling is then to choose a reference configuration where the formation energy is known, e.g. the one pure metal A in a binary A–B alloy, and to use the rescaling

$$t = t_{\text{MC}} \times C_V^{\text{MC}}(A) / C_V^{\text{eq}}(A)$$

where $C_V^{\text{MC}}(A)$ is now the vacancy concentration in pure A in the MC box (that can be measured in the MC simulations) and $C_V^{\text{eq}}(A) = \exp[-E_V^{\text{for}}(A)]$ is the equilibrium vacancy concentration in pure A.

Another possibility is to introduce in the simulation the point defect formation and elimination mechanisms, with their respective frequencies. This has been done recently to take into account the evolution of point defect concentrations during thermal ageing [11] or under irradiation [12].

3. Simulations of phase transformations in alloys

3.1. Simple examples of precipitation kinetics in binary alloys

The simplest case of diffusive phase transformations is probably the coherent precipitation of a second phase in a binary solid solutions with unmixing tendency during an isothermal annealing [1]. A typical example is the copper precipitation in dilute Fe–Cu alloys. The copper solubility in α -iron is small, with a maximum of 1.8 at.% at 850 °C. In supersaturated solid solutions, one observes a precipitation of coherent copper clusters which keep the body-centred cubic (bcc) structure of the iron matrix for radius up to 2 nm. During subsequent growth, precipitates pass through faulted structures (3R and 9R) and finally reach the perfect face-centred cubic (fcc) structure of the pure copper. Copper precipitation – which can be greatly accelerated under irradiation, due to the high point defect concentrations – has long been suspected to play a role in the hardening and embrittlement of some reactor pressure vessel (RPV) steels. It has motivated many experimental studies on copper precipitation in RPV steels and model alloys, both during thermal ageing or under electron, ion or neutron irradiation.

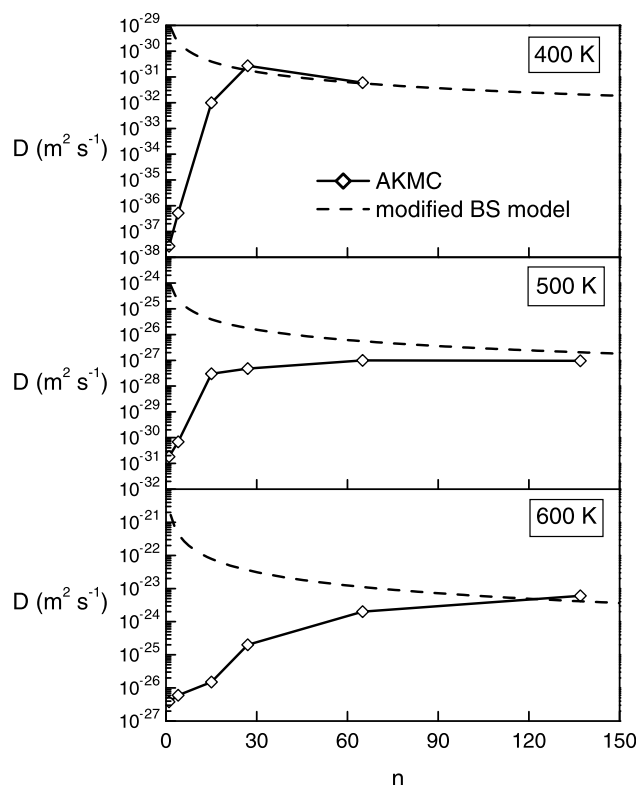


Fig. 2. Diffusion coefficients of clusters of n copper atoms measured by Monte Carlo simulations [13] at 400, 500 and 600 K. The dotted lines correspond to the prediction of a modified Binder–Stauffer model for large precipitate sizes.

Fig. 2. Coefficients de diffusion d'amas de n atomes de cuivre mesurés dans des simulations Monte Carlo [13] à 400, 500 et 600 K. La ligne pointillée correspond à la prédiction du modèle de Binder–Stauffer modifié, pour les grandes tailles d'amas.

Many AKMC simulations have been devoted to this system [13–19]. In Ref. [13] the AKMC parameters have been fitted on DFT calculations to model the copper precipitation kinetics in Fe–1.34 at.% Cu at various temperatures. Simulations are in good agreement with experimental results (Fig. 1). They reveal the formation of almost pure copper clusters from the very beginning of the precipitation. In the simulations, as shown by DFT calculations, the vacancy formation energy is much higher in bcc iron (~ 2.1 eV) than in bcc copper (~ 0.9 eV). As a result vacancy is strongly trapped in copper clusters, which become more mobile than individual copper atoms (Fig. 2). This favours direct coagulation between precipitates. This example also shows that AKMC simulations are frequently limited to the first precipitation steps: cluster dynamics and large scale KMC methods can be used for the latter ageing times (see below).

This influence of the vacancy diffusion mechanism on the precipitation pathway is not specific to Fe–Cu alloy. It has been evidenced in other AKMC simulations in model alloys. By controlling the migration of small solute clusters, atomic details of diffusion can strongly affect the nucleation stage [20,21], severely reducing the incubation period for instance, as well as the coarsening stage [15,22–26], going from a coarsening by evaporation and condensation of monomers to a direct coagulation mechanism. AKMC simulations also show that the atomic diffusion mechanism influences the morphology of precipitate interfaces [24,27] allowing sharp or diffuse interfaces according to vacancy kinetic properties.

Precipitation in Fe–Cr alloys has been also modeled with AKMC in the range of concentrations and temperature corresponding to the α – α' miscibility gap [28–30]. Solute concentration of 9–18 at.% Cr are thus higher than for the dilute Fe–Cu alloy. Precipitation kinetics correspond to a classical succession of nucleation, growth and coarsening stages in qualitative agreement with experimental data [29]. One special feature of Fe–Cr alloy is the inversion of ordering tendency: they tend to order for low Cr concentrations and the unmixing only appears at higher concentrations. This arises from magnetism and can be caught by a rigid lattice model with both chemical and magnetic interactions [31]. Kinetic Monte Carlo simulations remain to be performed with such an energy model: it will allow extending the range of concentrations and temperatures that can be modeled and identifying the role of magnetism in the precipitation kinetics.

AKMC simulations are not restricted to alloys with an unmixing tendency: one can also model ordering alloys. Such simulations, based on the vacancy diffusion mechanisms, have been used for instance to study the precipitation of the B2 phase in a model bcc alloy [32,33], or of the L_{12} phase in a model fcc alloy [34] or in Al–Sc and Al–Zr dilute alloys [35]. They show that ordering and phase separation proceed either concurrently or sequentially, depending on the atomic mobility parameters [32]. The L_{12} ordering of a model fcc A_3B alloy has been also investigated [36]: depending of the depth of the

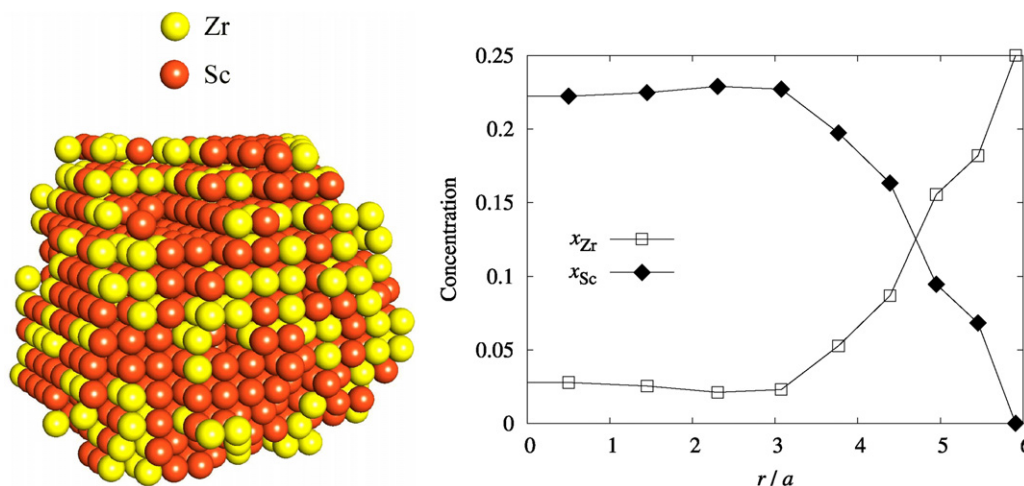


Fig. 3. $\text{Al}_3\text{Zr}_x\text{Sc}_{1-x}$ precipitate obtained by kinetic Monte Carlo simulation [39] of the annealing during 0.59 s at 550 °C of an aluminium solid solution containing 0.5 at.% Zr and 0.5 at.% Sc. The precipitate has the ordered L_{12} structure (for clarity, only Zr and Sc atoms are shown). The corresponding radial concentration profile shows the Zr enrichment of the periphery compared to the core of the precipitate.

Fig. 3. Précipité $\text{Al}_3\text{Zr}_x\text{Sc}_{1-x}$ obtenu par simulation Monte Carlo [39] d'un recuit de 0.59 s à 550 °C d'une solution solide d'aluminium contenant 0.5 at.% de Zr et 0.5 at.% de Sc. Le précipité a la structure ordonnée L_{12} (pour plus de clarté, seuls les atomes de Zr et de Sc sont représentés). Le profil de concentration radial correspondant montre l'enrichissement en Zr à la périphérie du précipité par rapport au cœur.

temperature quench, an incubation time is observed or the ordering proceeds by spinodal decomposition. Incubation times obtained with a set of parameters representative of Cu_3Au agree with experimental ones [36].

3.2. Homogeneous precipitation in multicomponent alloys

The kinetics pathways are often much more complex in ternary than in binary alloys, particularly when the diffusion coefficients of the various solute atoms strongly differ. When the difference between solute diffusivities is small, the system can reduce its free energy by following the line of highest slope and precipitates are formed with a composition close to the equilibrium one. A typical case is the formation of ordered γ' precipitates (Ni_3X with an L_{12} structure), in Ni–Cr–Al alloys [37,38], where AKMC simulations predict classical nucleation–growth–coarsening sequences, in good agreement with experimental observations using 3D atom probes. Nevertheless, even in that case the coupling between fluxes of vacancies, Ni, Cr and Al at the γ/γ' interfaces is found to drive small transient deviations from the equilibrium compositions [38], leading to a slight Ni and Cr accumulation at the interface. Moreover, AKMC simulations have revealed that the vacancy diffusion mechanism is responsible of the interconnection by necks of adjacent precipitates which has been also observed with 3D atom probe tomography [38].

On the contrary, in Al–Zr–Sc dilute alloys Sc atoms diffuse much more rapidly than Zr atoms. According to AKMC simulations [39], the L_{12} precipitates mainly grow by absorbing Sc atoms at the beginning and their composition is close to the Al_3Sc one – even if it does not correspond to the highest driving force. Only when the Al matrix is depleted in Sc, precipitates grow by absorbing Zr atoms. As there is no diffusion in the ordered phase, a heterogeneous structure survives at the end of the precipitation, with a Sc-rich core surrounded by a Zr-rich shell (Fig. 3). Moreover, due to Zr slow diffusion, the external Zr-enriched shell is quite stable and prevents the precipitates from coarsening. This heterogeneous structure of the precipitates has been observed experimentally by high-resolution electron microscopy, by 3D atom probe and by small angle X-ray diffraction. Atomic simulations also show that a Zr addition to an Al–Sc alloy leads to an increase of the precipitate density associated with a decrease of their size, still in agreement with experimental observations. This Zr addition is responsible of a higher nucleation driving force, and therefore more precipitates nucleate. As precipitates mainly grow then by absorbing Sc atoms and less Sc is available for the growth of each nucleus at the end of the nucleation stage, one obtained smaller precipitates which do not coarsen because of the Zr enriched external shell.

Large difference in solute mobilities is a common situation in steels, where small solute atoms C and N diffuse by direct interstitial jumps, much more rapidly than substitutional atoms, which require neighboring vacancy to diffuse. A typical example has been modelled in Fe–Nb–C alloys, where the difference of diffusivity between Nb and C strongly affects the kinetics pathway: for low supersaturations, a direct precipitation of equilibrium NbC precipitates is observed in AKMC simulations, whereas transient iron carbides are formed before NbC precipitates appear for higher supersaturations [11,40].

Interaction of solute atoms with vacancy can also affect the precipitation pathway. AKMC simulations [41] show that Mg addition to Al–Cu and Al–Li–Cu alloys leads to the formation of small Mg–Cu–vacancy complexes because of the strong binding between Mg and vacancy as well as between Mg and Cu. These small complexes act as heterogeneous nucleation sites for Guinier–Preston (GP) zones and accelerate the precipitation kinetics. In agreement with 3D atom probe observations in Al–Zn–Mg–Cu alloys, the small GP zones observed in the simulations are richer in Mg than the larger ones [42]. This

binding of Mg to vacancies is also responsible of the migration of Mg-rich clusters, leading to a coalescence mechanism in the coarsening stage [42].

Heterogeneous precipitation on pre-existing solute cluster is another scenario which can happen in multicomponent alloys. For instance, an enhancement of the copper precipitation by a Ni or a Mn addition has been experimentally observed in iron alloy thanks to hardness measurements and 3D atom probe tomography [43]. AKMC simulations [43] show that this enhancement arises from heterogeneous precipitation of the Cu atoms on Ni and Mn clusters which appear during the cooling down after the stress relief treatment at high temperature.

3.3. Heterogeneous precipitation and elasticity

Precipitation occurs more frequently on the extended defects of the alloy microstructure, such as grain boundaries and dislocations. The modelling of this situation is more difficult, since the formation free energy of precipitates depends on the atomic structure of the defect. A rigid lattice approximation cannot fully take into account such details, but it can nevertheless reproduce some key features of heterogeneous precipitation: the segregation tendencies of solute atoms at dislocations or grain boundaries and the decrease of formation free energy, the local acceleration of diffusion, the long range interaction between dislocations and solute atoms, etc.

Such AKMC simulations have been developed to study NbC precipitation in α -iron both at grain boundaries [44] and dislocations [45]. Elasticity could be partly accounted for in these simulations by considering the size interaction between solutes and the dislocation strain field. This strain field contributes to solute segregation on the dislocation and therefore strongly enhances heterogeneous precipitation. Similar AKMC simulations have been performed in model fcc alloys to study the formation of Cottrell atmospheres on dislocation junctions and its effect on the strength of the junction thanks to dislocation dynamics simulations [46].

To have a better account of all elastic effects, in particular the microstructure relaxation along the kinetic path, one needs to give up the rigid lattice description and to adopt continuous description of the energy with the variations of the atomic positions. Empirical potential offers then a compromise. Due to the necessity to calculate on-the-fly the point defect migration barriers at every time step, such relaxed AKMC simulations are restricted on timescales much smaller than a precipitation kinetics. These simulations have been used for instance to study the clustering onset in a phase separating Al–Cu alloy [47], vacancy diffusion in disordered Au–Ni alloys [48] and in silicon [49], or anelasticity (Snoek peak) associated with C in iron [50].

3.4. Precipitation under irradiation

AKMC simulations are especially useful to model phase transformations under irradiation. Radiation damage results in the formation and diffusion of specific point defects, such as self-interstitial atoms with typical and complex “dumbbell” configurations, which are difficult to fully take into account in diffusion models [51]. More fundamentally, alloys submitted to permanent irradiation are a special case of driven systems, for which no general theory is still available. In such systems, the diffusion mechanisms not only affect the kinetics of the transformation, but the steady-state the alloy can reach depending on the irradiation conditions [52] (contrary to thermal systems, where diffusion mechanisms affect the kinetics of the system, but not its equilibrium state).

AKMC simulations have been used to study the competition between disorder produced in displacement cascades (the so-called “ballistic mixing”), which tends to dissolve the precipitates, disorder ordered phases, and suppress concentration gradients; and thermally activated diffusion mechanisms, which tend to bring back the alloy towards its equilibrium states [53,54]. Another phenomena of great technological importance is radiation induced segregation, which results from the elimination of excess point defects, produced by irradiation, on the sinks available in the microstructure of the alloy (dislocations, surfaces, grain boundaries). These fluxes of point defects produce fluxes of solutes and a modification of the alloy composition near the sinks. If the solute composition reaches the solubility limit, a heterogeneous radiation induced precipitation can be observed in an undersaturated solid solution [55].

AKMC simulations can be used to measure the coupling coefficients between flux of atoms and defects, e.g. for fluxes of copper and vacancies in iron [56,57] or to model the evolution of the alloy microstructure under irradiation [12,58–60,10]. Homogeneous radiation induced precipitation has been observed in the simulations of Ref. [61], according to the mechanism predicted by Caivin and Martin in Refs. [62,63]. In case of positive coupling between the flux of solute atoms and both the fluxes of vacancies and interstitials, the mutual recombination of point defects can sustain an additional flux of solute atoms towards already solute enriched regions. This leads to the destabilisation of the solid solution.

4. Validation and improvement of mesoscopic models

Whatever the efficiency of the algorithms, the needed computational time remains a severe drawback of AKMC simulations of precipitation. This atomic approach is often restricted to the study of the precipitation onset, like nucleation and the beginning of growth, and to the high supersaturations. Indeed, AKMC cannot replace mesoscopic modeling techniques, with all their rationalising power, to address longer aging times. These mesoscopic models are based on classical descriptions of the different precipitation stages, either nucleation, growth and coarsening, or spinodal decomposition. The ease

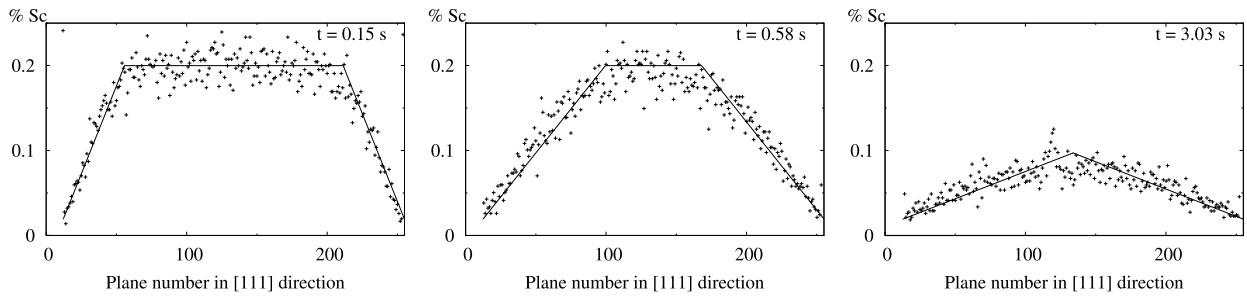


Fig. 4. Kinetic evolution of a concentration profile in an Al–Sc supersaturated solid solution at $T = 450^\circ\text{C}$ in contact with a plane Al_3Sc precipitate. The dots are obtained by kinetic Monte Carlo simulations [35] and the solid lines by a classical growth model.

Fig. 4. Évolution cinétique du profil de concentration dans une solution solide Al–Sc sursaturée, en contact avec un précipité plan Al_3Sc à 450°C . Les points sont obtenus par simulations Monte Carlo cinétique [35] et les lignes continues par un modèle de croissance classique.

of their implementation in fast algorithms makes them the suitable tools to model precipitation in an industrial context. Their predicting ability can be nevertheless quite poor because of the uncertainty of the assumptions they rely on and of their input parameters which are seldom perfectly known. Atomic simulations allow understanding the main ingredients that have to be caught by their mesoscopic modeling, as well as calculating unambiguously their input parameters. These leads to a multiscale approach where mesoscopic models validated on atomic simulations are used to extrapolate the range of supersaturations and timescales that can be simulated. Several examples of this approach are given below.

4.1. Classical nucleation theory

Classical nucleation theory (CNT) [64] allows predicting the nucleation rate, i.e. the density of new nuclei appearing per unit of time, in a supersaturated binary solid solution. A comparison with AKMC simulations [20] shows that it correctly predicts the nucleation rate in a metastable solid solution with an unmixing tendency as long as only monomers can migrate and other solute clusters are immobile. For an ordering solid solution, like Al–Zr or Al–Sc alloys, a good agreement is obtained between both modeling scales as long as the alloy ordering tendency is considered when computing the nucleation driving force needed as input by CNT [35,65]. This contrasts with the way this theory is usually applied: the ideal or regular solid solution approximations generally used in combination with CNT cannot lead to quantitative predictions, and one has to rely on more sophisticated thermodynamic approximation like the cluster variation method or low temperature expansions.

4.2. Precipitate growth

Classically, two different kinetic regimes can be considered for the growth of a precipitate [1]. The growth-limiting process can be either the reaction at the interface to attach one more atom on the precipitate, or the long-range diffusion of solute atoms from the matrix. In this last case, one assumes that the solute concentration at the interface between the precipitate and the matrix is the equilibrium one, and the precipitate growth rate is obtained by solving the diffusion problem. One can use kinetic Monte Carlo simulations so as to see which growth regime is the correct one. An example is given in Fig. 4 for the growth of a plane Al_3Sc precipitate in a supersaturated solid solution, showing that the growth is controlled by the long-range diffusion. The concentration profile observed in atomic simulations in the direction perpendicular to the precipitate interfaces is in perfect agreement with the one deduced from diffusion equations linearised to first order in concentration gradient using the impurity diffusion coefficient, thus validating a classical description of the precipitate growth.

4.3. Cluster dynamics

Cluster dynamics (CD) [64] offer a way to model at a mesoscopic scale the whole precipitation kinetics, including the nucleation, the growth and the coarsening stages in the same framework. Precipitation is described through the time evolution of the cluster size distribution, which is governed by rate equations corresponding to the absorption by a cluster and the evaporation from a cluster of monomers. The input parameters are the precipitate interface free energies and the growing rate of the precipitates. A comparison between precipitation kinetics obtained with AKMC and CD, both in the case of an unmixing tendency (Fe–Cu alloy [69]) and an ordering tendency (Al–Zr and Al–Sc alloys [66]) shows that a quantitative agreement can be obtained between both modeling techniques as long as the size dependence of the precipitate interface free energy is taken into account.

CD simulations can be used to model precipitation kinetics at time much larger than allowed by AKMC simulations. It thus allows to extrapolate the precipitation kinetics to aging time compatible with experiments. Fig. 5 shows that CD simulations manage to reproduce both results of AKMC simulations for short aging times, and experimental data for longer times in precipitating Al–Sc alloys.

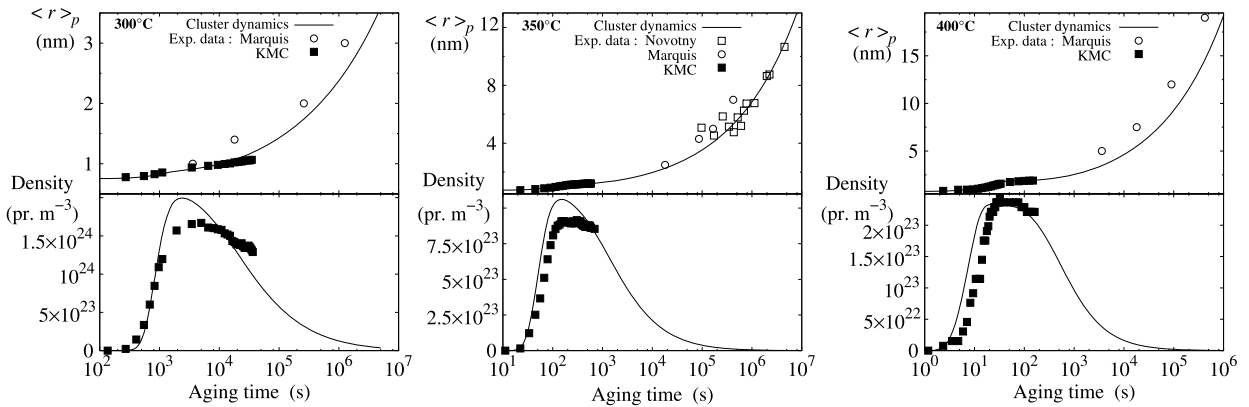


Fig. 5. Mean precipitate radius and precipitate density as a function of the aging time for an aluminium solid solution containing 0.18 at.% Sc as given by AKMC [35], CD [66] and experimental data [67,68].

Fig. 5. Rayon moyen et densité moyenne des précipités en fonction du temps de recuit d'une solution solide d'aluminium contenant 0.18 at. % de Sc, d'après les simulations Monte Carlo cinétique [35], la dynamique d'amas [66] et les données expérimentales [67,68].

Another interesting case of interplay between the atomic and the mesoscopic scale is the modeling of copper precipitation in iron. The mobility of small clusters revealed by AKMC simulations (cf. Section 3.1) can be easily handled by CD simulations [69], as well as by mesoscale KMC simulations based on similar approximations [70] as CD. These mesoscale simulations show that the cluster mobility plays a strong role in the precipitation by speeding up the whole kinetics. They now match experimental kinetics while using a more realistic value for the diffusion coefficient of copper in iron than previous CD simulations where only monomers were assumed to diffuse.

Finally, the confrontation with AKMC simulations allows extending CD modeling to more concentrated alloys [71], going beyond the dilute limit where simulations were initially restricted.

5. Conclusion

AKMC simulations provide a convenient way to simulate and model precipitation kinetics in alloys. Thanks to a precise description of diffusion at the atomic scale they can predict a variety of different kinetic behaviours. Interaction of solute atoms with the vacancy, for instance, has been shown to influence the mobility of small precipitates, and, as a consequence, the way nucleation, growth and coarsening proceed. Such atomic simulations are even more useful in multicomponent alloys or in alloys under irradiation where the precipitation pathway is not only driven by thermodynamics but can be strongly affected by diffusion. It is thus possible to predict the formation of transient compounds or precipitation of out-of-equilibrium structures. Once the kinetics pathway has been fully characterised at the atomic scale thanks to these simulations, one can build mesoscopic modeling that extends the range of supersaturations and annealing times that can be simulated.

References

- [1] Georges Martin, The theories of unmixing kinetics of solid solutions, in: *Solid State Phase Transformations in Metals and Alloys*, Les Éditions de Physique, Orsay, 1978, pp. 337–406.
- [2] Richard Wagner, Reinhard Kampmann, Peter W. Voorhees, Homogeneous second-phase precipitation, in: Gernot Kosterz (Ed.), *Phase Transformations in Materials*, 2005, pp. 309–407.
- [3] Kurt Binder, Peter Fratzl, Spinodal decomposition, in: Gernot Kosterz (Ed.), *Phase Transformations in Materials*, les Éditions de Physique, Orsay, 2005, pp. 409–480.
- [4] Mark E.J. Newman, G.T. Barkema, *Monte Carlo Methods in Statistical Physics*, Oxford University Press, 1999.
- [5] David P. Landau, Kurt Binder, *A Guide to Monte Carlo Simulations in Statistical Physics*, Cambridge University Press, 2005.
- [6] J. Philibert, *Atom Movements: Diffusion and Mass Transport in Solids*, Les Éditions de Physique, Orsay, 1991.
- [7] W.M. Young, E.W. Elcock, Monte Carlo studies of vacancy migration in binary ordered alloys: I, *Proc. Phys. Soc. London* 89 (1966) 735–746.
- [8] A.B. Bortz, M.H. Kalos, J.L. Lebowitz, A new algorithm for Monte Carlo simulation of Ising spin systems, *J. Comput. Phys.* 17 (1975) 10–18.
- [9] Georges Martin, Frédéric Soisson, Kinetic Monte Carlo method to model diffusion controlled phase transformations in the solid state, in: Sidney Yip (Ed.), *Handbook of Materials Modeling*, Springer, The Netherlands, 2005, pp. 2223–2248.
- [10] C.S. Becquart, C. Domain, Introducing chemistry in atomistic kinetic Monte Carlo simulations of Fe alloys under irradiation, *Phys. Status Solidi B* 247 (2010) 9–22.
- [11] D. Gendt, Cinétiques de précipitation du carbure de niobium dans la ferrite, PhD thesis, Université de Paris XI, Orsay, 2001.
- [12] Frédéric Soisson, Kinetic Monte Carlo simulations of radiation induced segregation and precipitation, *J. Nucl. Mater.* 349 (2006) 235–250.
- [13] Frédéric Soisson, Chu Chun Fu, Cu-precipitation kinetics in α -Fe from atomistic simulations: Vacancy-trapping effects and Cu-cluster mobility, *Phys. Rev. B* 76 (2007) 214102.
- [14] F. Soisson, G. Martin, A. Barbu, Copper precipitation in dilute iron–copper alloys: A Monte Carlo simulation, *Ann. Phys. (Paris)* 20 (3) (June 1995) 13–20.
- [15] F. Soisson, A. Barbu, G. Martin, Monte Carlo simulations of copper precipitation in dilute iron–copper alloys during thermal ageing and under electron irradiation, *Acta Mater.* 44 (1996) 3789–3800.
- [16] S. Schmauder, P. Binkele, Atomistic computer simulation of the formation of Cu-precipitates in steels, *Comput. Mater. Sci.* 24 (1–2) (2002) 42–53.

- [17] P. Binkle, S. Schmauder, An atomistic Monte Carlo simulation of precipitation in a binary system, *Z. Metallkd.* 94 (8) (August 2003) 858–863.
- [18] E. Vincent, C.S. Becquart, C. Domain, Solute interaction with point defects in [alpha] Fe during thermal ageing: A combined ab initio and atomic kinetic Monte Carlo approach, *J. Nucl. Mater.* 351 (1–3) (2006) 88–99.
- [19] E. Vincent, C.S. Becquart, C. Pareige, P. Pareige, C. Domain, Precipitation of the FeCu system: A critical review of atomic kinetic Monte Carlo simulations, *J. Nucl. Mater.* 373 (1–3) (2008) 387–401.
- [20] F. Soisson, G. Martin, Monte-Carlo simulations of the decomposition of metastable solid solutions: Transient and steady-state nucleation kinetics, *Phys. Rev. B* 62 (2000) 203–214.
- [21] Y. Le Bouar, F. Soisson, Kinetics pathway from embedded-atom-method potential: Influence of the activation barriers, *Phys. Rev. B* 65 (2002) 0914103.
- [22] P. Fratzl, O. Penrose, Competing mechanisms for precipitate coarsening in phase separation with vacancy dynamics, *Phys. Rev. B* 55 (1997) R6101–R6104.
- [23] M. Athènes, P. Bellon, G. Martin, Effects of atomic mobilities on phase separation kinetics: a Monte-Carlo study, *Acta Mater.* 48 (2000) 2675–2688.
- [24] Jean-Marc Roussel, Pascal Bellon, Vacancy-assisted phase separation with asymmetric atomic mobility: Coarsening rates, precipitate composition, and morphology, *Phys. Rev. B* 63 (2001) 184114.
- [25] R. Weinkamer, P. Fratzl, By which mechanism does coarsening in phase-separating alloys proceed? *Europhys. Lett.* 61 (2003) 261.
- [26] Richard Weinkamer, Peter Fratzl, Himadri S. Gupta, Oliver Penrose, Joel L. Lebowitz, Using kinetic Monte Carlo simulations to study phase separation in alloys, *Phase Transitions* 77 (2004) 433–456.
- [27] Jean-Marc Roussel, Pascal Bellon, Interface sharpening and broadening during annealing of Cu/Ni multilayers: A kinetic Monte Carlo study, *Phys. Rev. B* 73 (2006) 085403.
- [28] Pär Olsson, Janne Wallenius, Christophe Domain, Kai Nordlund, Lorenzo Malerba, Two-band modeling of α -prime phase formation in Fe–Cr, *Phys. Rev. B* 72 (2005) 214119.
- [29] G. Bonny, D. Terentyev, L. Malerba, D. Van Neck, Early stages of α – α' phase separation in Fe–Cr alloys: An atomistic study, *Phys. Rev. B* 79 (2009) 104207.
- [30] C. Pareige, C. Domain, P. Olsson, Short- and long-range orders in Fe–Cr: A Monte Carlo study, *J. Appl. Phys.* 106 (2009) 104906.
- [31] M.Yu. Lavrentiev, D. Nguyen-Manh, S.L. Dudarev, Magnetic cluster expansion model for bcc–fcc transitions in Fe and Fe–Cr alloys, *Phys. Rev. B* 81 (2010) 184202.
- [32] M. Athènes, P. Bellon, G. Martin, F. Haider, A Monte-Carlo study of B2 ordering and precipitation via vacancy mechanism in b.c.c. lattices, *Acta Mater.* 44 (1996) 4739–4748.
- [33] D. Le Floc'h, P. Bellon, M. Athènes, Slow coarsening of B2-ordered domains at low temperatures: A kinetic Monte Carlo study, *Phys. Rev. B* 62 (2000) 3142–3152.
- [34] T.A. Abinandanan, F. Haider, G. Martin, Computer simulations of diffusional phase transformations: Monte Carlo algorithm and application to precipitation of ordered phases, *Acta Mater.* 46 (1998) 4243–4255.
- [35] E. Clouet, M. Nastar, C. Sigli, Nucleation of Al_3Zr and Al_3Sc in aluminium alloys: from kinetic Monte Carlo simulations to classical theory, *Phys. Rev. B* 69 (2004) 064109.
- [36] M. Kessler, W. Dieterich, A. Majhofer, Ordering kinetics in an fcc A_3B binary alloy model: Monte Carlo studies, *Phys. Rev. B* 67 (2003) 134201.
- [37] C. Pareige, F. Soisson, G. Martin, D. Blavette, Ordering and phase separation in Ni–Cr–Al: Monte Carlo simulations vs three-dimensional atom probe, *Acta Mater.* 47 (1999) 1889–1899.
- [38] Zugang Mao, Chantal K. Sudbrack, Kevin E. Yoon, Georges Martin, David N. Seidman, The mechanism of morphogenesis in a phase-separating concentrated multicomponent alloy, *Nat. Mater.* 6 (2007) 210–216.
- [39] E. Clouet, L. Laé, T. Epicier, W. Lefebvre, M. Nastar, A. Deschamps, Complex precipitation pathways in multicomponent alloys, *Nat. Mater.* 5 (2006) 482–488.
- [40] Dominique Gendt, Philippe Maugis, Georges Martin, Maylise Nastar, Frédéric Soisson, Monte Carlo simulation of NbC precipitation kinetics in α -Fe, *Defect Diff. Forum* 194–199 (2001) 1779–1786.
- [41] S. Hirosawa, T. Sato, A. Kamio, H.M. Flower, Classification of the role of microalloying elements in phase decomposition of Al based alloys, *Acta Mater.* 48 (2000) 1797–1806.
- [42] G. Sha, A. Cerezo, Kinetic Monte Carlo simulations of clustering in an Al–Zn–Mg–Cu alloy (7050), *Acta Mater.* 53 (2005) 907–917.
- [43] A. Cerezo, S. Hirosawa, I. Rozdilsky, G.D.W. Smith, Combined atomic-scale modelling and experimental studies of nucleation in the solid state, *Philos. Trans. R. Soc. London A* 361 (2003) 463–477.
- [44] C. Hin, Y. Bréchet, P. Maugis, F. Soisson, Kinetics of heterogeneous grain boundary precipitation of NbC in α -iron: A Monte Carlo study, *Acta Mater.* 56 (2008) 5653–5667.
- [45] C. Hin, Y. Bréchet, P. Maugis, F. Soisson, Kinetics of heterogeneous dislocation precipitation of NbC in α -iron, *Acta Mater.* 56 (2008) 5535–5543.
- [46] Q. Chen, X.-Y. Liu, S.B. Biner, Solute and dislocation junction interactions, *Acta Mater.* 56 (2008) 2937–2947.
- [47] D.R. Mason, R.E. Rudd, A.P. Sutton, Atomistic modelling of diffusional phase transformations with elastic strain, *J. Phys.: Condens. Matter* 16 (2004) S2679.
- [48] J.L. Bocquet, On-the-fly evaluation of diffusional parameters during a Monte Carlo simulation of diffusion in alloys: a challenge, *Defect Diff. Forum* 203–205 (2002) 81–112.
- [49] Fedwa El-Mellouhi, Normand Mousseau, Laurent J. Lewis, Kinetic activation–relaxation technique: An off-lattice self-learning kinetic Monte Carlo algorithm, *Phys. Rev. B* 78 (2008) 153202.
- [50] Sébastien Garruchet, Michel Perez, Modelling the carbon Snoek peak in ferrite: Coupling molecular dynamics and kinetic Monte-Carlo simulations, *Comp. Mater. Sci.* 43 (2008) 286–292.
- [51] A.R. Allnatt, A.B. Lidiard, *Atomic Transport in Solids*, Cambridge University Press, October 2003.
- [52] G. Martin, P. Bellon, Driven alloys, *Solid State Phys.* 50 (1997) 189–331.
- [53] Raül A. Enrique, Pascal Bellon, Compositional patterning in systems driven by competing dynamics of different length scale, *Phys. Rev. Lett.* 84 (13) (March 2000) 2885.
- [54] Raül A. Enrique, Pascal Bellon, Compositional patterning in immiscible alloys driven by irradiation, *Phys. Rev. B* 63 (13) (March 2001) 134111.
- [55] A.J. Ardell, Radiation-induced solute segregation in alloys, in: *Materials Issues for Generation IV Systems*, 2008, pp. 285–310.
- [56] A.V. Barashev, A.C. Arokiam, Monte Carlo modelling of Cu atom diffusion in α -Fe via the vacancy mechanism, *Philos. Mag. Lett.* 86 (5) (2006) 321.
- [57] F. Soisson, C.C. Fu, Atomistic simulations of copper precipitation and radiation induced segregation in α -iron, *Solid State Phenom.* 139 (2008) 107.
- [58] J. Rottler, D.J. Srolovitz, R. Car, Kinetic Monte Carlo study of radiation-induced segregation in model metallic alloys, *Philos. Mag.* 87 (2007) 3945.
- [59] P.R. Monasterio, B.D. Wirth, G.R. Odette, Kinetic Monte Carlo modeling of cascade aging and damage accumulation in Fe–Cu alloys, *J. Nucl. Mater.* 361 (2007) 127–140.
- [60] E. Vincent, C.S. Becquart, C. Domain, Microstructural evolution under high flux irradiation of dilute Fe–CuNiMnSi alloys studied by an atomic kinetic Monte Carlo model accounting for both vacancies and self interstitials, *J. Nucl. Mater.* 382 (2008) 154–159.
- [61] P. Krasnochtchekov, R.S. Averback, P. Bellon, Homogeneous phase separation in binary alloys under ion irradiation conditions: Role of interstitial atoms, *Phys. Rev. B* 75 (2007) 144107.

- [62] R. Cauvin, G. Martin, Solid solutions under irradiation. I. A model for radiation-induced metastability, *Phys. Rev. B* 23 (7) (April 1981) 3322.
- [63] R. Cauvin, G. Martin, Solid solutions under irradiation. 2. Radiation-induced precipitation in AlZn undersaturated solid solutions, *Phys. Rev. B* 23 (7) (1981) 3333–3348.
- [64] Emmanuel Clouet, Modeling of nucleation processes, in: D.U. Furrer, S.L. Semiatin (Eds.), *Fundamentals of Modeling for Metals Processing*, in: ASM Handbook, vol. 22A, ASM, 2009, pp. 203–219.
- [65] Emmanuel Clouet, Maylise Nastar, Classical nucleation theory in ordering alloys precipitating with $L1_2$ structure, *Phys. Rev. B* 75 (2007) 132102.
- [66] Emmanuel Clouet, Alain Barbu, Ludovic Laé, Georges Martin, Precipitation kinetics of Al_3Zr and Al_3Sc in aluminium alloys modeled with cluster dynamics, *Acta Mater.* 53 (2005) 2313–2325.
- [67] E.A. Marquis, D.N. Seidman, Nanoscale structural evolution of Al_3Sc precipitates in Al–Sc alloys, *Acta Mater.* 49 (2001) 1909–1919.
- [68] G.M. Novotny, A.J. Ardell, Precipitation of Al_3Sc in binary Al–Sc alloys, *Mater. Sci. Eng. A* 318 (2001) 144–154.
- [69] T. Jourdan, F. Soisson, E. Clouet, A. Barbu, Influence of cluster mobility on Cu precipitation in α -Fe: A cluster dynamics modeling, *Acta Mater.* 58 (2010) 3400–3405.
- [70] T. Jourdan, J.-L. Bocquet, F. Soisson, Modeling homogeneous precipitation with an event-based Monte Carlo method: Application to the case of Fe–Cu, *Acta Mater.* 58 (2010) 3295–3302.
- [71] J. Lépinoux, Modelling precipitation in binary alloys by cluster dynamics, *Acta Mater.* 57 (2009) 1086–1094.