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Kinetic Monte Carlo Simulations of Precipitation**

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We present some recent applications of the atomistic diffusion model and of the kinetic Monte Carlo (KMC) algorithm to systems of industrial interest, i.e. Al-Zr-Sc and Fe-Nb-C alloys, or to model systems. These applications include study of homogeneous and heterogeneous precipitation as well as of phase transformation under irradiation. The KMC 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.

1. Introduction

At the atomic scale, the kinetic Monte Carlo (KMC) simulation technique is the suitable tool to study diffusion-controlled phenomena like precipitation kinetics in crystalline alloys. Thanks to a precise description of the equilibrium and diffusion properties which control the evolution of the alloy, such simulations can predict the kinetic pathways in full details. These predictions are valuable for multi-component alloys because few information on the precipitation kinetics is available whereas the diversity of the possible kinetic pathways is richer than for a binary alloy. From a fundamental point of view, such simulations are also useful to test and improve other larger scale modelling techniques.

After a brief description of the atomistic diffusion model and of the KMC algorithm, we present some recent applications to systems of industrial interest, i.e. Al-Zr-Sc and Fe-Nb-C alloys, or to model systems. These applications include study of homogeneous and heterogeneous precipitation as well as of phase transformation under irradiation. The KMC 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.

2. Principles of Kinetic Monte Carlo Simulations

The KMC simulation method that we use has been already thoroughly reviewed in different papers.[1–3] Here, we only present its main principles.

2.1. Atomic Diffusion Model

If we restrict the model to coherent phase transformations, i.e. transformations which keep the underlying lattice the same, precipitation is nothing but jumps of atoms from site to site on the lattice. Interstitial atomic species can jump in any neighbouring interstitial site as long as it is empty, whereas substitutional atomic species need a neighbouring vacancy to exchange with it. All these events are thermally activated: whenever an atom jumps, changing the configuration of the alloy from C to C', the probability per unit time for the transition to occur writes

$$W_{\mathrm{C}\to\mathrm{C}'} = \nu^0_{\mathrm{C}\to\mathrm{C}'} \exp(-E^{\mathrm{act}}_{\mathrm{C}\to\mathrm{C}'}/kT), \tag{1}$$

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where $\nu^0_{C\rightarrow C}$ and $E^{act}_{C\rightarrow C'}$ are respectively the attempt frequency and the activation energy of the jump, k is the Boltzmann's constant and T the temperature. The activation energy is computed as the difference between the total energy of the system when the jumping atom is at the saddle-point position and the total energy of the system before the jump. As the system remains coherent, a simple broken bond model can be used to express $E^{act}_{C\rightarrow C'}$: the energy of the stable configuration is written as a sum of interactions between atoms (Ising model), which implies that $E^{act}_{C\rightarrow C'}$ is the difference between the binding energy of the jumping atom at the saddle point position and the sum of all interactions corresponding to broken bonds during the jump. The interactions of the Ising model are adjusted so as to reproduce equilibrium properties of the system. The other parameters of this atomic diffusion model are the binding energy of the atoms at the saddle point positions and the attempt frequencies $\nu^0_{C\rightarrow C'}$: they are fitted so as to reproduce diffusion coefficients. Note that these different parameters can be deduced too from ab-initio calculations instead of being fitted to experimental data.

2.2. Residence Time Algorithm

Being given an atomic diffusion model, the KMC method relies on the residence time algorithm. At each Monte Carlo step, different events can occur in the simulation box: vacancies can exchange with one of their neighbours or interstitials can jump. The frequency of each of these events is computed with the help of Equation 1 and the next configuration C' of the system is chosen according to the probability law $\tau_C W_{C\rightarrow C'}$, where τ_C is the time spent by the system in the configuration C and is given by

$$\tau_C = 1/\Sigma_{C'} W_{C\rightarrow C'}. \qquad (2)$$

This algorithm provides then the kinetic pathway of the alloy, i.e. the sequence of configurations the system will go through and the time at which it reaches each configuration.

3. Homogeneous Precipitation

3.1. Al-Zr-Sc Alloys

Zr and Sc precipitate in aluminium alloys to form the $Al_3Zr_xSc_{1-x}$ compound, which for low super-saturations of the solid solution, exhibits the $L1_2$ structure. Using experimental data (Zr and Sc solubility limits and diffusion coefficients in aluminium) as well as ab-initio results (Al_3Zr and Al_3Sc enthalpy of formation as well as Zr-Sc interaction in aluminium), we developed an atomic diffusion model for Al-Zr-Sc relying on a rigid lattice with pair interactions between first and second nearest neighbours.[4–6] All atomic species are substitutional and therefore diffusion occurs only by exchange with vacancies. The KMC simulations predict that $L1_2$ precipitates are inhomogeneous: their core is richer in Sc than in Zr whereas this is the opposite for the external shells (Fig. 1). This structure given by our atomic model agrees with experimental observations recently made with high resolution electron microscopy[7] and with three-dimensional atom probe.[8–10] It arises from the kinetic behaviour of the Al-Zr-Sc alloy: Sc diffuses much more faster than Zr in aluminium (about 1000 times faster at the considered temperatures). Therefore a nucleated precipitate grows by absorbing first Sc and then Zr when the solid solution becomes depleted in Sc. As there is no diffusion inside the precipitates, their structure is a direct consequence of their formation history. This inhomogeneous structure explains why $L1_2$ precipitates are less sensitive to coarsening in the ternary Al-Zr-Sc than in the binary Al-Sc alloy.

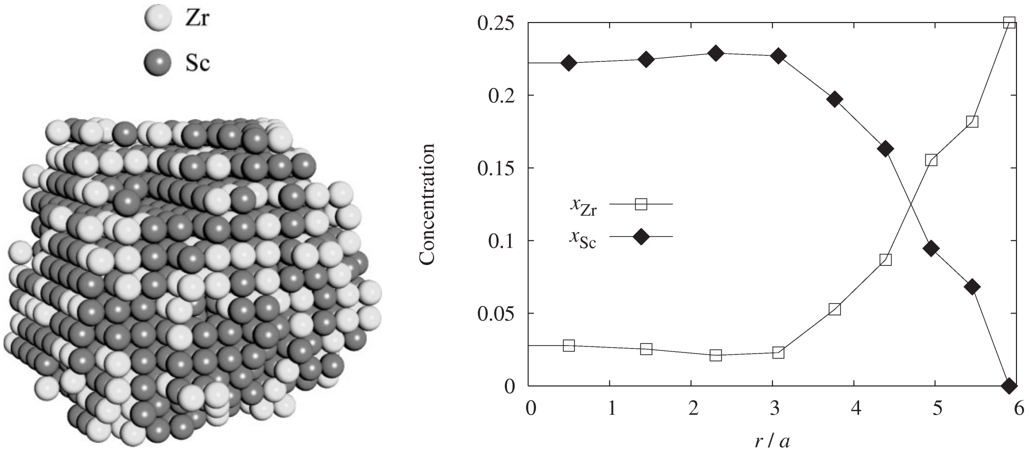

Fig. 1. $L1_2$ precipitate obtained after the annealing during 0.59 s at 550 °C of an aluminium solid solution containing 0.5 at.% Zr and 0.5 at.% Sc simulated with KMC (for clarity, only Zr and Sc atoms are shown). The corresponding radial concentration profile shows the Zr enrichment of the periphery compared to the core of the precipitate.

3.2. Fe-Nb-C Alloys

In high-strength steels, niobium addition leads to hardening by NbC precipitation. This implies the migration of both Nb, by vacancy mechanism, and C, by direct interstitial mechanism. An atomic diffusion model has been built for Fe-Nb-C, considering these two diffusion mechanisms.[11,12] Due to the presence of C interstitial atoms, a lot of possible events have to be considered at each step of the KMC simulations, which requires to modify the residence time algorithm. For low super-saturated solid solutions, one observes a direct precipitation of NbC clusters with the classical nucleation-growth-coarsening sequence. But for high super-saturations, simulations reveal the possibility for NbC nucleation to be preceded by the formation of a transient iron carbide, due to rapid diffusion of C atoms by comparison with Nb and Fe diffusion (Fig. 2).

The kinetic pathway is found to be sensitive to the ability of the microstructure to provide the proper equilibrium vacancy concentration during the precipitation process. It is highlighted by introducing a simple model of vacancy source and sink in the atomic diffusion model. Some new events, which correspond to a vacancy formation or annihilation on the sink/source, are introduced in the simulations with probabilities which tend to maintain the equilibrium concentration.

3.3. Other Systems of Industrial Interest

Among other alloys where homogeneous precipitation was studied with KMC, one can cite copper precipitation in ferrite.[13,14] Simulations brought out the migration of small Cu clusters which leads to direct coagulation between precipitates instead of classical emission-adsorption of single atoms. In Ni-Al-Cr alloys, a good agreement was found between the simulated precipitated structure and the one observed with three-dimensional atom probe.[15]

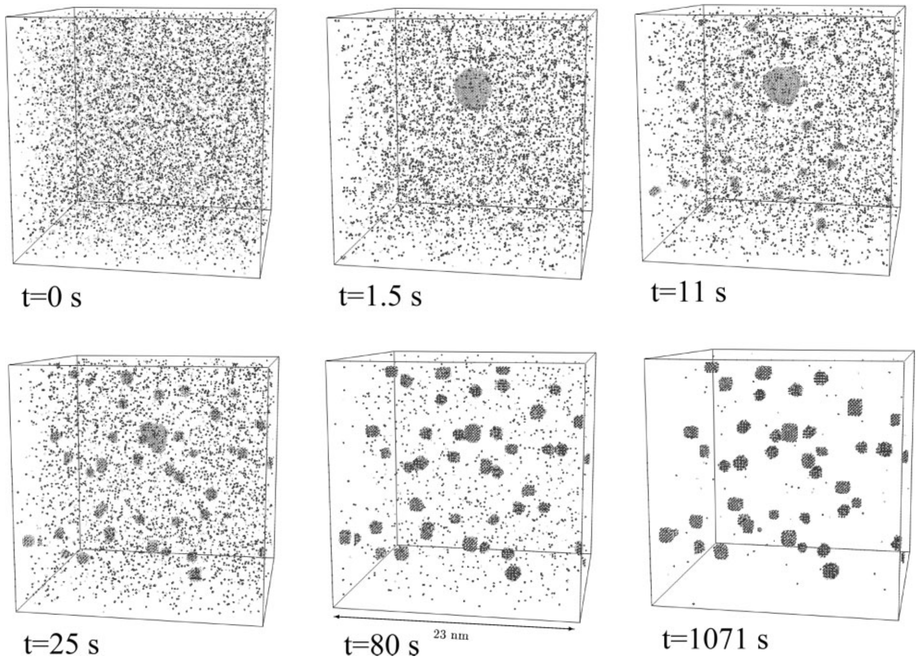

Fig. 2. KMC simulation of NbC precipitation in ferrite (Fe-0.5 at.%Nb-0.5 at.%C) during thermal aging at T=627 °C. A transient precipitation of a metastable iron carbide is observed at 1.5, 22 and 25 sec. Nb and C atoms are respectively represented in red and gray, and Fe atoms belonging to the iron carbide in yellow.

4. Heterogeneous Precipitation

The atomic diffusion model previously presented for Fe-Nb-C has been extended so as to study heterogeneous precipitation on grain boundaries[16] and on dislocations.[17] In the simulations, the grain boundary is modelled as a plane where a segregation energy adjusted on experimental data is imposed for C and Nb. Acceleration of diffusion along the grain boundary is also considered, but no deformation of the lattice nor disorientation between the two grains is taken into account. During the KMC simulations, one observes a first stage where the fast diffusing C atoms segregate on the grain boundary and precipitate to form metastable iron carbides (Fig. 3). In a second stage, Nb segregates too, leading to the formation of NbC nuclei inside the iron carbides. These iron carbides then shrink to the benefit of the equilibrium NbC ones which grow. For low super-saturations, only this scenario of heterogeneous precipitation is observed (Fig. 3(a)), whereas for higher super-saturations a direct nucleation/growth of the NbC precipitates occurs in the bulk too (Fig. 3(b)). Due to enhanced diffusion, precipitates are larger at the grain boundary than in the bulk.

To study heterogeneous precipitation on dislocations, a dislocation is introduced in the simulation box by imposing segregation energies on a line of sites. On the other atomic sites, an interaction energy which is decreasing as the inverse of the distance with the dislocation is added so as to consider the long range elastic field. This long range field is found to strongly favour heterogeneous precipitation.[17]

5. Phase Transformation Under Irradiation

A precise description of diffusion mechanisms is even more important under irradiation, since they control not only the kinetics towards the equilibrium state, but the steady-state itself an alloy can reach.

In addition to the previous vacancy and direct interstitial jumps, new events are expected under irradiation. Nuclear collisions result in "displacement cascades" (small disordered regions of few nanometers

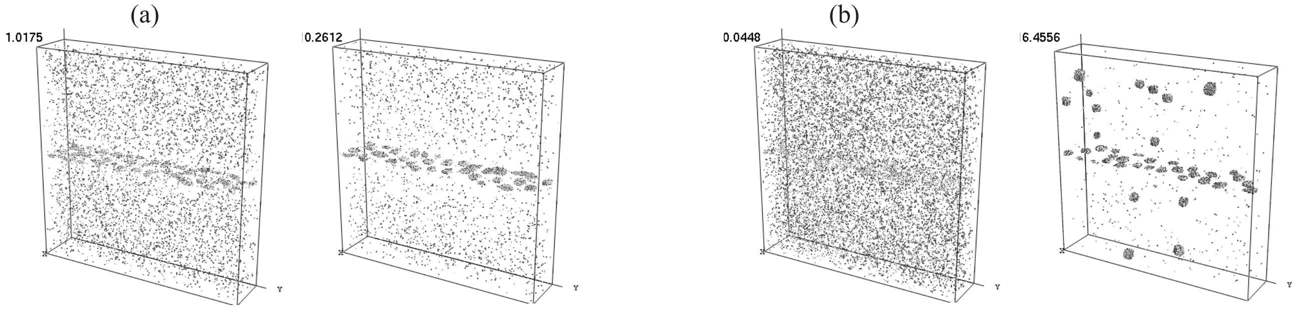

Fig. 3. KMC simulations of NbC heterogeneous precipitation at a grain boundary in ferrite during thermal aging at T=727 °C for two different compositions: (a): Fe-0.3 at.%Nb-0.3 at.%C; (b): Fe-0.5 at.%Nb-0.5 at.%C. A transient precipitation of metastable iron carbides is observed at the grain boundary located at the middle height of the simulation box. Nb and C atoms are respectively represented in purple and gray, and Fe atoms belonging to the iron carbide in yellow.

where the different elements are mixed together), which tend to homogenize the alloy configuration. On the other hand the same collisions create a lot of point defects (both vacancies and self-interstitial atoms the latter usually with a "dumbbell" configuration). Most of them disappear by mutual recombination or annihilation at sinks, but the point defect concentrations nevertheless exceed equilibrium concentrations (often by several order of magnitude), leading to a general acceleration of diffusion.

As a result, phase transformation kinetics under irradiation is often controlled by the balance between disordering events, which tends to dissolve precipitates and to disorder intermetallic compounds, and the acceleration of diffusion, which tends to drive the system towards its equilibrium state and then to accelerate precipitation and ordering kinetics. The former effect is dominant at lower temperatures (when point defect migration is slow), and the later at higher temperatures.[18]

Another common phenomena is radiation induced segregation, which can also induce phase transformations, even at low radiation fluxes. Since point defect concentrations exceed equilibrium ones, permanent fluxes of vacancies and self-interstitial atoms are sustained towards sinks such as free surfaces, grain boundaries, dislocations, etc. They are balanced by atomic fluxes (in the same direction for the interstitials, in the opposite one for the vacancies) and this leads to a local modification of the alloy composition. If the local solute concentration reaches the solubility limit, one observes radiation induced precipitation. This coupling between point defects and solute fluxes, and thus the precipitate microstructure, are of course very dependent on the atomic scale diffusion mechanisms. Point defect creation, recombination, migration and annihilation at sinks have been introduced in Monte Carlo simulations to model radiation induced segregation.[19] A simple example is displayed on Figure 4: under irradiation, point defects are created throughout an under saturated solid solution A-B. Close vacancy-interstitial pairs recombine, and surviving defects migrate towards a grain boundary located in the middle of the simulation box (it is simply modelled as a plane of lattice sites which act as perfect point defect sinks). In that particular case B atoms are slower than A atoms by the vacancy mechanism ($D^v_B<D^v_A$) and faster by the interstitial one ($D^i_B>D^i_A$): as a consequence, the solute concentration increases near the grain boundary and rapidly reaches the solubility limit. An almost *B* pure layer nucleates and growths with the radiation dose (expressed in dpa – displacement per atom and per second).

6. Comparison with Classical Kinetic Theories

One drawback of KMC simulations is the needed computational time which imposes to study high super-saturations and short annealing times. This is not the case for mesoscopic model based on classical descriptions of the nucleation, growth and coarsening stages. These models require input parameter (the nucleation and the interface free energy, the diffusion coefficients, $\cdots$) which can be computed from the atomic diffusion model. As these models are widely used for industrial purpose, it is interesting to test them and to improve their description of precipitation thanks to a direct comparison with KMC simulations. For instance, it was

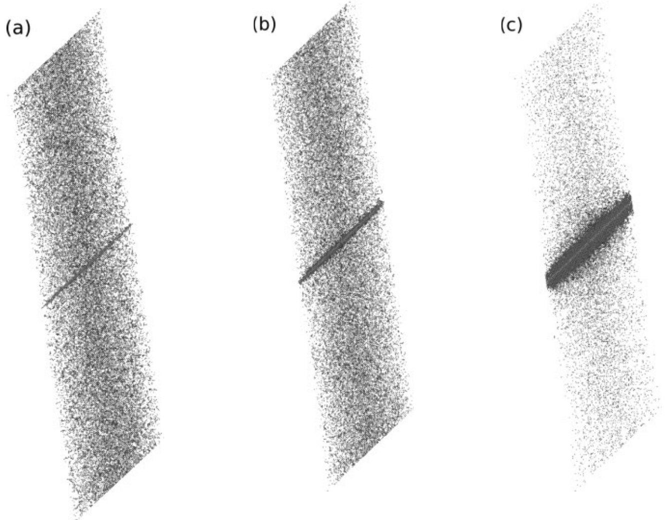

Fig. 4. Evolution of an under saturated A-B alloy (solute concentration C_B=0.05, solubility limit C_B^{eq}=0.08) under a radiation flux G=10^{-6} dpa.s^{-1} at T=527 °C, in the case $D_B^v<D_A^v$ and $D_B^i>D_A^i$. Microstructure is observed at (a)2.46 × 10^{-3}, (b) 2.02 × 10^{-2} and (c) 1.20 dpa. A grain boundary is located in the middle of the simulation box (grey dots). The black dots correspond to B solute atoms, A atoms are omitted. [19]

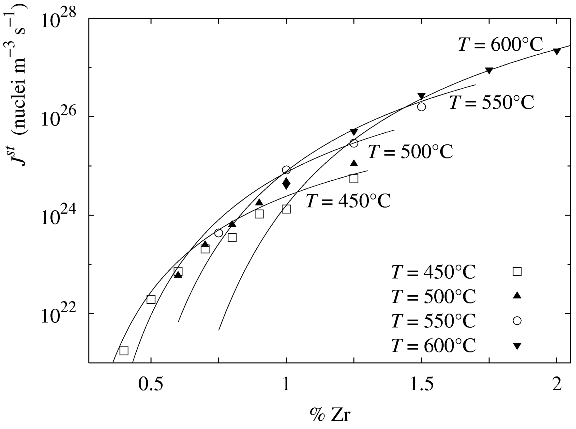

Fig. 5. Variation with the nominal concentration and the temperature of the steady-state nucleation rate J^{st} for Al_3Zr precipitation. Symbols correspond to KMC simulations and lines to CNT.

shown for a model bcc alloy with an unmixing tendency that the decomposition of a metastable solid solution was correctly described by classical nucleation theory (CNT) as long as only monomers can migrate and other solute clusters are immobile.[20] For Al-Zr and Al-Sc binary alloys,[4–6] one has to consider the short range order when computing the nucleating free energy so as to obtain a good agreement between CNT and KMC simulations (Fig. 5). The cluster variation method or a low temperature expansion can be used to calculate this parameter, but the ideal or regular solid solution models are irrelevant for these ordering alloys.

7. Conclusion

KMC simulations based on a simple atomic diffusion model are shown to be very useful to study homogeneous or heterogeneous precipitation, in particular the nucleation stage. In multi-component alloys, such simulations can reveal unsuspected kinetic pathways. They also allow the improvement of classical descriptions for the different precipitation stages.

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