MULTI-SCALE MODELLING OF THE MICROSTRUCTURE EVOLUTION APPLIED TO PWR MATERIALS

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1. INTRODUCTION

The evolution of materials properties such as the yield strength, hardness or ductile to brittle transition is directly dependent on the materials microstructure. Under irradiation, because of the arrival of energetic particles such as neutrons, numerous point defects (vacancies and Self Interstitial Atoms (SIAs)) are created whose evolution with time will induce many changes in the microstructure. Typical examples are formation of dilute solute clusters containing Cu, Ni, Mn, Si observed in the bainitic steels constituting the pressure vessel reactors or Cr depletion at the grain boundaries in the stainless steels of the internals. This paper gives an overview of the strategy followed nowadays to model the evolution of metallic alloy microstructures under irradiation conditions. The development of numerical tools capable of simulating the effects of radiation on mechanical properties of materials is becoming more and more wide-spread because of on the one hand side the increasing costs of the experiments and on the other hand the increasing power of computer. Usually these numerical tools are linked within a multi-scale platform. This is the approach followed, for instance, by the European, and wider, international scientific community created around the FP6 PERFECT and FP7 PERFORM60 projects for in service fission reactors.
The multi-scale approach draws its name because one has to resort to different simulation techniques as many length and time scales are involved in the different events taking place, which can be schematically summarised as follows: the impinging neutrons decelerate in the material through a succession of collisions (called displacement cascades initiated by the Primary Knocked-on Atom (PKA)) which create SIAs and vacancies, isolated or in small clusters as the energy transfer in the ballistic collision is several orders of magnitude larger than the Frenkel Pair energy formation (i.e. the formation energy of a vacancy and a SIA in the crystal). The point defects can diffuse, recombine or agglomerate leading to larger defects such as dislocation loops or cavities. These larger defects can, for instance, interact with the dislocations of the microstructure, acting as obstacles to dislocation motion, thus inducing hardening. Under specific conditions, Franck loops can unfault, thus enhancing significantly their mobility. The glissile loops thus generated can strengthen the initial dislocation network or on the contrary annihilate, thus inducing a softening of the initial dislocation network. When significant fluxes of point defects towards sinks are sustained, the growth of vacancy clusters can induce the formation of voids or cavities which cause swelling. The production of He causes by transmutation reactions can then play a role in this synergy by stabilizing the vacancy clusters. Finally, the preferential binding of alloying elements with point defect fluxes can lead to local redistributions of the elements and thus changes of the compositions locally.

The series of events described above take place within different time and spatial scales and requires thus different modelling techniques. For instance, displacement cascades occur at the picosecond time scale and the damage region is few tenths of nanometers. The most appropriate method to model these events is classical molecular dynamics (MD) used with simulation boxes containing a few million atoms. The subsequent evolution of the point defects thus created need to be tackled using other techniques. Indeed, the simulation of the evolution of atoms and the dynamics of a piece of crystal requires in principle to simulate the atomic vibrations. The typical order of the atomic vibrations frequencies is 10^{13} Hz and the time step for the integration of the Newton equations is usually close to 1 fs. At the time and length scale of MD simulations, the diffusion of point defects, SIAs and vacancies can be considered as a " non frequent event" in which the system makes an occasional transition from one configuration to another one. This event is equivalent to a transition from a potential basin to another one, and the rate constants can be determined from transition state theory. This activation process is associated to fractions of ns up to ns or ms depending on the temperature and activation energy. MD is thus no more adapted and mesoscale techniques such as kinetic Monte Carlo methods are developed and applied. In these techniques, the elementary physical mechanism is

the migration of atoms, via point defects for substitutional atoms, without considering explicitely the atomic vibrations. These methods take into account the position of the defects and are limited to a few hundred of nm system size. Different KMC methods are used depending on the physical phenomena simulated which cover different time and spatial scales.

The different steps of a multi-scale modelling scheme aiming at predicting the microstructure evolution of irradiated materials can thus be summarized as follows **(figure 1)**:

- Step 0: from neutrons to PKA's spectrum
- Step 1: from PKA's spectrum to displacement cascades
- Step 2: from (sub)cascades to the primary damage
- Step 3: from the primary damage to experimentally resolvable defects
- Step 4: from the experimentally resolvable defects to the yield stress

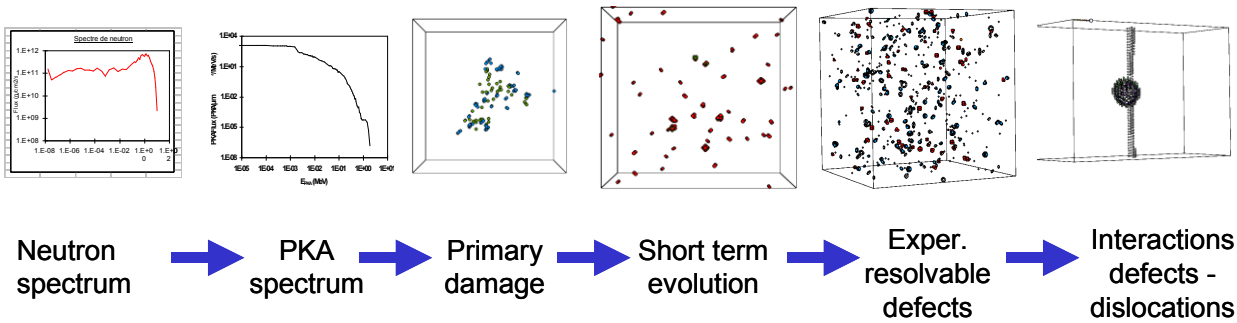


Figure 1: modelling the microstructure

In the following, we first describe briefly the different bricks of the multi-scale approach for modelling the evolution of the microstructure under radiation conditions. We then provide a short presentation of the different techniques employed nowadays as well as a short discussion on the validation of the approach.

2. THE MULTISCALE APPROACH

Modelling the microstructural evolution of metallic materials under radiation damage conditions requires thus to investigate the different following situations:

The first event is the arrival of energetic particles, the predominant ones being neutrons which interact with matter. The neutrons transfer part of their energy to a few atoms called the Primary Knock-on Atoms (PKAs) which will be ejected from their lattice sites, collide with neighbour atoms and create displacement cascades. Several codes can be used to calculate the primary recoil spectra, weighted recoil spectra, displacement cross sections induced by electrons, ions and neutrons. In the case of the PERFECT project, the PKA spectrum which gives the number of PKAs created by time and volume units obtained from the neutron spectrum is determined by SPECTER which calculates spectral- averaged displacements, recoil spectra, gas production, and total damage energy for around 40 pure elements using the ENDF/B-V database of nuclear data derived cross sections. The only input from the user is the neutron energy spectrum. As SPECTER does not handle compounds, displacement damage for alloys, insulators, and breeder materials need to be handled by SPECOMP. Both softwares can be found on the NEA web site. Another program, DART, based on the binary collision approximation was developed recently to calculate primary recoil spectra, weighted recoil spectra and displacement cross sections induced by electrons, ions and neutrons in solids. It is based on recent nuclear evaluations containing accurate angular distributions of recoils for all neutron atom interactions. For these different codes, the accuracy of the neutron cross section database, as input, is crucial.

In principle, one should simulate displacement cascades for every damage energy of the PKA spectrum. This task is not feasible by MD for very high energy PKAs. This can be overcome considering that, the PKAs induce displacement cascades which may split into sub-cascades if their energies are high enough. For high PKA energies, where the Binary Collision Approximation (BCA) holds, the mean free path between two high energy collisions (which is proportional to the inverse cross-section) is large compared to the cascade extension. So one usually models finite number of low energy PKAs, using MD, to obtain the primary damage, i.e. the amount and distribution of the point defects created.

The evolution of the point defects created by the PKAs, their interactions with the solute atoms as well as with other elements lead to the evolution of the microstructure and thus to the property changes of the materials. To extend the study up to the formation of experimentally resolvable damage features (point defect clusters, dislocation loops, solute precipitates...), one turns to computational tools based on Kinetic Monte Carlo (KMC) or on Mean Field Rate Theory (MFRT). These codes produce size distributions of experimentally resolvable defects (voids, loops, precipitates …), including defects with sizes lower than the resolution achievable experimentally.

The interaction of defects with dislocations is a fundamental but not completely solved problem which should strictly be studied at the atomic level. It is most of the time tackled with the use of MD which allows to determine the binding energies and pinning forces between dislocations and each type of hardening defect at the atomic scale. The forces can then be used as input data in a Foreman and Makin type model where the defects are introduced as a 3D array of obstacles to the motion of a dislocation within its glide plane. The dislocation line shape is defined by the equilibrium between the tension line, the applied stress and the pinning forces. The applied stress makes the dislocation glide and bow between the pinning defects. The maximum stress applied gives the local yield stress increase due to the irradiation induced defects. Algorithms to simulate Dislocation Dynamics (DD) appeared in the 90's. In these methods, the collective behaviour of an ensemble of dislocations is modelled by determining the forces on each dislocation and taking into account all the possible reactions between dislocations as well as the other elements of the microstructure. The dislocation lines are described as flexible strings, sequences of short rigid segments. The segments can have one or more integration points for force calculations and they can be on a network or not. The dislocations are created, move, join and change shape as a consequence of applied stress and mutual interactions described using elasticity theory. DD simulations allow to predict the relative increase of critical resolved shear stress due to the radiation damage created defects.

Finally constitutive laws describing the flow behaviour in a mathematical form are then derived, as flow behaviour is the basic information which allows the computation of stresses and strains acting in a material under an applied load. The whole sequence, as it is applied to model steels under radiation damage conditions is summarized in **figure 2**.

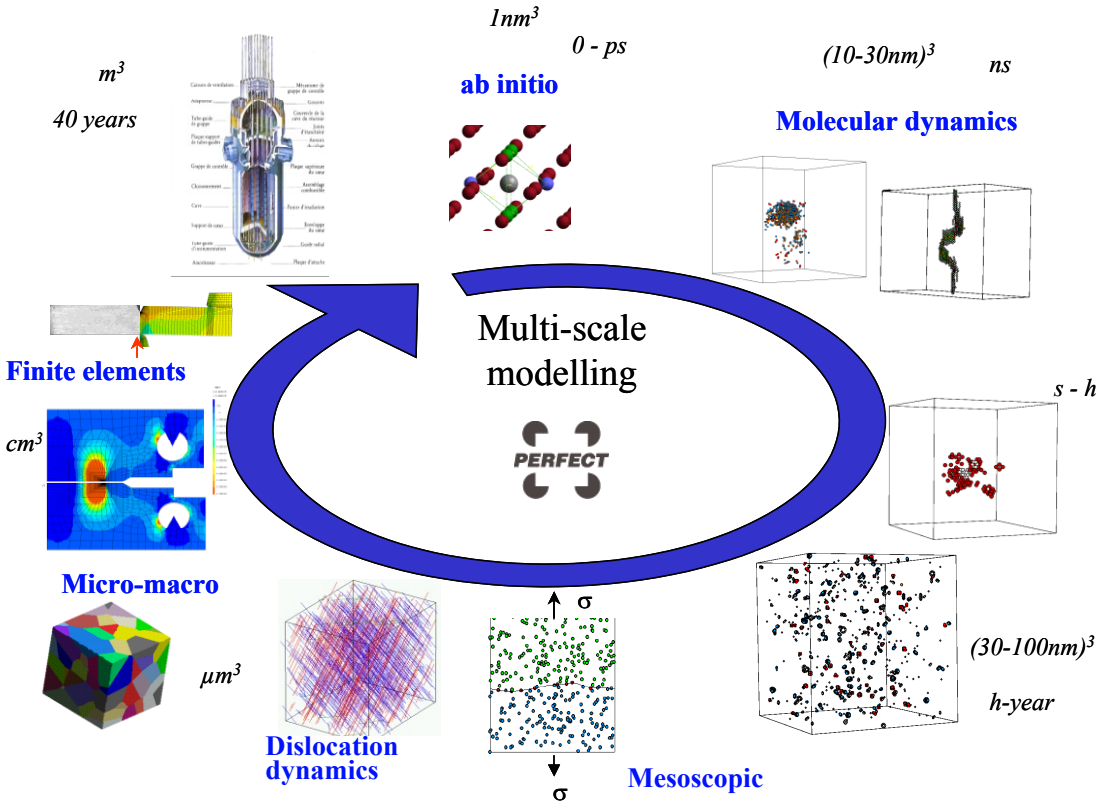


Figure 2: multiscale modelling scheme applied within the PERFECT and PERFORM60 projects to the pressure vessel bainitic steels and internal austenitic steels.

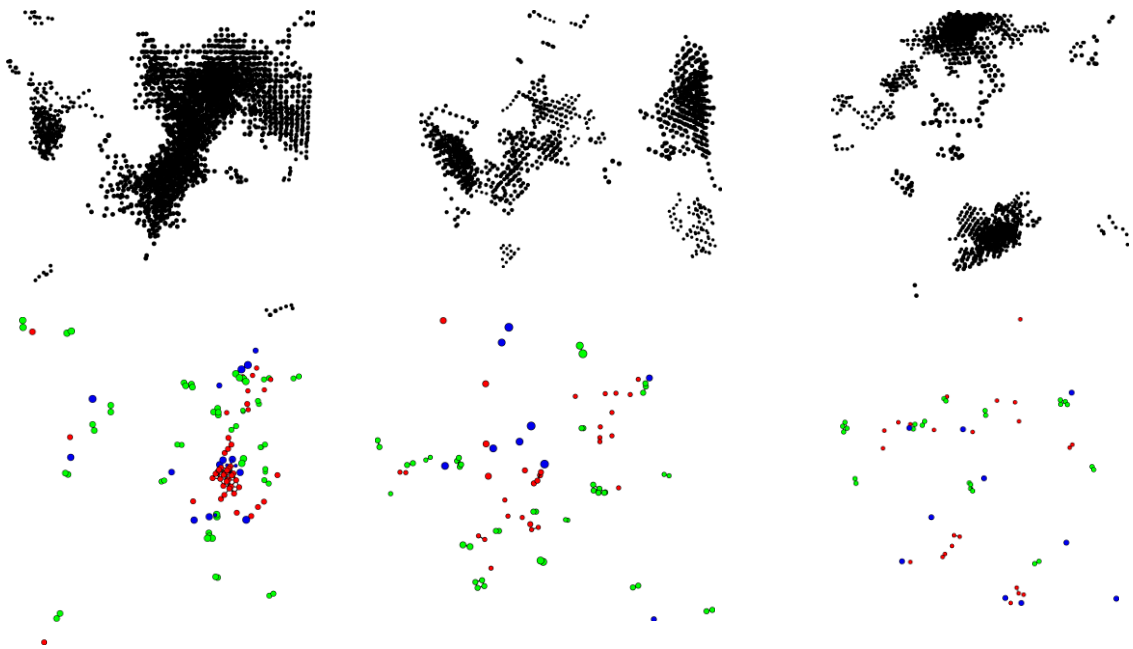
3. SIMULATION TECHNIQUES

3.1 Molecular dynamics – primary damage

Molecular Dynamics (MD) is a technique, originally developed in the 50's, and nowadays used by a great number of scientists, particularly in materials science. MD is based on Newton's mechanics: the properties of a group of atoms or particles are obtained by computing the trajectories of each particle in time. For that purpose, the atoms are considered as point masses and Newton's law $\vec{f}_i = m_i \vec{a}_i$ (where $\vec{f}_i$ is the sum of the forces felt by atom i, m_i its mass and $\vec{a}_i$ its acceleration). MD is is the most appropriate method to simulate the primary damage and to characterise the properties of point defect and point defect clusters (e.g. their stability, their mobility and how they interact). Unlike first principles calculations, MD codes are easy to program and many groups use their in-house developed software. However, many all purposes MD codes are available to simulate molecules for instance or proteins. LAMMPS (Large-scale Atomic/Molecular Massively Parallel Simulator), XMD and DYMOKA are more materials oriented. Codes such as DYMOKA, MOLDY, MDCASK, DLPOLY provide the essential features to simulate the primary damage.

The simulation of the primary damage formation is initiated by giving one atom, the PKA, a momentum corresponding to energies varying from 1 to a few hundred keV. The choice of the simulation box size depends upon the energy of the PKA. It must be large enough to avoid the displacement cascade to interfere with itself by periodic overlap. Before initiating the displacement cascade, the system of particles is let to equilibrate, for a few ps, at the chosen temperature. The simulations can be done in the micro canonical ensemble with periodic boundary conditions, or at constant pressure. At the beginning of the collision phase, the time-step has to be carefully monitored in order to keep the total energy constant. It is usually taken to be of the order of 10^{-17} s and can be increased to 10^{-15} s during the cooling down of the cascade. In metals, some common approximations are often made such as not taking into account the electron-phonon coupling and not damping the boundary atoms to extract heat or attenuate the out-going pressure wave. One usually agrees on the fact that the final simulation temperature rise scarcely influences the defect population generated in displacement cascades.
The construction of the cohesive model, i.e. the interatomic potential is the critical point. Most of the time, an analytical formalism is chosen with some fitting parameters adjusted on some elementary and/or target properties. The transferability of the potential depends on the input properties fitted on, and the more different and out off equilibrium these input properties and/or configurations the better the potential can be expected to be.

Figure 3 depicts the primary damage produced by a 10 keV PKA in FeNi alloys of various concentrations. The presence of the Ni changes the morphology of the cascade as well as the number of residual defects, showing the significance of alloying on the primary damage formation.



35 at. % Ni 75 at. % Ni 100 at. % Ni

Figure 3: MD modelling of the primary damage. 10 keV displacement cascades in FeNi at 600 K (327 Celsius). Top figures : atoms replaced (i.e. which have left their initial site), bottom figures : residual defects. The red spheres are vacancies, the blue ones are self interstitial atoms and the green ones are dumbbells.

3.2 Kinetic Monte Carlo methods and Mean Field Rate Theory – evolution of the primary damage to experimentally resolved defects

The evolution of the primary damage is due to the diffusion of point defects and solute atoms. These phenomena are driven by thermally activated jumps, with activation energies between few tenths of eV and a few eV and cannot be modelled using MD techniques. Indeed, MD typically uses time steps of the order of ~10^{-15} s to obtain an accurate integration of the atomic motion which limits the total duration of the simulations to less than one microsecond, while relevant thermally activated processes typically take place over time scales of microseconds or even longer. The number of jumps diffusing species can experience is thus very limited: a few tenth jumps for a C atom at 1000°C. As a consequence, it is clear that the long range diffusion of atoms and the long term evolution of the microstructure are not in the range of MD simulations specially at the operating temperatures of the structural components. To extend the study up to the formation of experimentally resolvable damage features (point defect clusters, dislocation loops, solute precipitates...), MFRT and KMC techniques are used. KMC methods treat objects (OKMC), events (EKMC) or atoms (AKMC) in a specific volume.

The KMC methods are MC methods which can be classified as rejection-free in contrast with the more classical MC methods based on the Metropolis algorithm. The KMC methods provide a solution to the Master Equation which describes a physical system whose evolution is governed by a known set of transition rates between possible states. The solution proceeds by choosing randomly among the various possible transitions and accepting them on the basis of probabilities that depend directly on the corresponding transition rates. KMC methods have the advantage of going beyond the mean field approximation by explicitly accounting for spatial correlations between the elements of the physical system and the overall geometry of the system. They can be applied to study the evolution of systems of mobile species, such as atoms in AKMC or larger defects, formed for instance under irradiation in so called coarser-grained KMC models such as OKMC for example. In OKMC models defect migration jumps are explicitly treated and reactions occur when two defects (mobile objects) meet each other, or meet traps and/or sinks. Event KMC are alternative models, where individual migration jumps are not treated explicitly. Most of the KMC techniques are based on the residence time algorithm (RTA) derived fifty years ago by Young and Elcock to model the diffusion of a vacancy in ordered alloys. Its basics is the following: for a system in a given state, instead of making a number of unsuccessful attempt to perform a transition to reach another state, as in the case of the Metropolis algorithm, one computes the average time the system remains in its state. One then performs one of the possible transitions according to its weight and determines the time it took for this transition to take place. According to standard transition state theory, the frequency Γ_x of a thermally activated event x such as a vacancy jump in an alloy (AKMC) or the jump of a void (OKMC) can be expressed as:

$$\Gamma_X = \nu_X \exp\left(-\frac{E_a}{k_B T}\right) \tag{1}$$

where ν_X is the attempt frequency, k_B is Boltzmann's constant, T the absolute temperature and E_a is the activation energy of the jump. During the course of the simulation, the probabilities of all the possible transitions are calculated and one of them is chosen, at each time-step, by extracting a random number, according to its probability. The associated time-step length δt and average time-step length Δt is given by:

$$\delta t = \frac{-\ln r}{\sum_n \Gamma_X} \qquad \Delta t = \frac{1}{\sum_n \Gamma_X} \tag{2}$$

where r is a random number between 0 and 1. KMC methods can provide a description of the amount and position of solute and point defect cluster evolution with time (**Fig.4**).

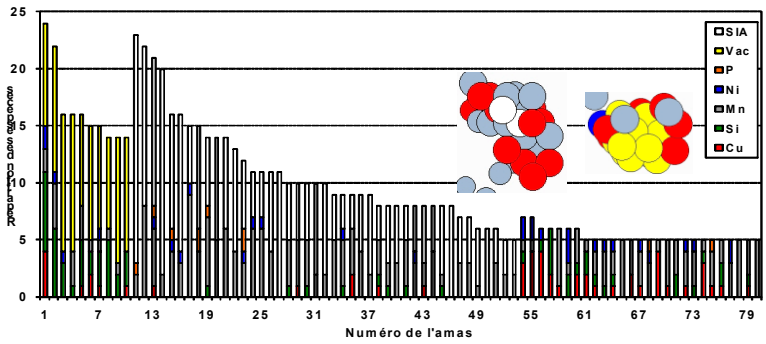
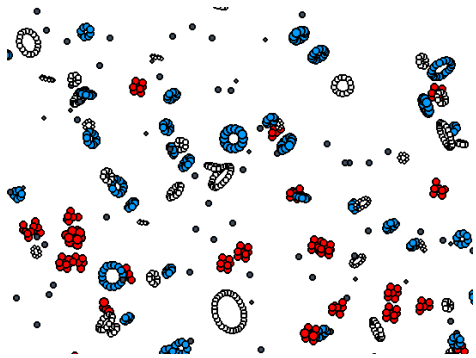


Figure 4: AKMC: point defect and solute cluster formed in 0.18Cu 1.38Mn 0.69Ni 0.43Si 0.01P at 18 mdpa at 300°C



OKMC: vacancy clusters and interstital loops at 300°C at 0.1 dpa of neutron irradiated bcc Fe.

RT methods are analytical methods in which a set of N coupled differential equations of balance is solved. They are known as mean-field techniques as only defect concentrations are taken into account and spatial inhomogeneities are not treated. The advantage is that without having to take the volume into account the computing time is much shorter than KMC computing times.

For the evolution of the concentration of single vacancy c_V, the equation is of the form:

$$\frac{dc_V}{dt} = K_V - k_V^2 D_V c_V - \alpha c_I c_V \tag{3}$$

The first term on the right hand side corresponds to the production rate of the mono-vacancies, the second term concerns the disappearance of the vacancies at sinks (the dislocation network, grain boundaries...) and the third one characterises the recombination of the vacancies with SIAs. K_V is the production rate of mono-vacancies, D_V is the diffusion coefficient of the mono-vacancy, k_V^2 is the sink strength, c_I the concentration of SIAs. Similar equations have to be solved for each cluster family. When solute atoms are taken into account, clusters of (n) point defects and (p) solute (labelled (n,p)) can be formed. The reaction taken into account are: the capture of a cluster (m,q) by a cluster (n,p) (characterised by adsorption coefficients B), and the emission of single defects or single defect – solute complexes (characterised by emission coefficients A). The set of equations can be generalised as follows:

$$\begin{aligned}\frac{dC(n,p)}{dt} = K(n) \\ - A((n,p),(\pm 1,0/1)) \cdot C(n,p) \\ + A((n \pm 1, p + 0/1),(\pm 1,0/1)) \cdot C(n \pm 1, p + 0/1) \\ + \sum_{(m,q)} B((n-m, p-q),(m,q)) \cdot C(n-m, p-q) \cdot C(m,q) \\ - \sum_{(m,q)} B((n,p),(m,q)) \cdot C(n,p) \cdot C(m,q) \\ - S(n,p)\end{aligned} \tag{4}$$

The first term of the equation corresponds to the source term calculated by decomposition of the PKA spectrum. (±1,0/1) stands for all the single defects and single defect-solute atoms pairs than can be emitted according to the model: SIA (+1,0), vacancy (-1,0), self interstitial – solute (+1,1) and vacancy – solute (-1,1). The second term corresponds to the rate of emission by (n,p), it depends on the coefficient A, which is a function of the cluster geometry. Similarly, the third term correspond to a positive contribution in the rate of increase *dC(n,p)/dt* of (n,p) clusters due to neighbouring cluster classes ((n+1,p), (n-1,p), (n+1,p+1) and (n-1,p+1)) defect emissions. The fourth term stands for defect adsorption resulting in the production of (n,p) clusters, while the fifth term accounts for the destruction of (n,p) by adsorption of an (m,q), which results in the production of an (n+m, p+q) cluster. Note that the two sums must be performed only on possible (m,q) values, an adsorption reaction requires that at least one of the reacting clusters is mobile. The last term accounts for cluster sinks which can be the dislocation network, or the grain boundaries.

These discrete set of rate equations are then numerically integrated. When large system are considered, e.g. large values of n (several hundreds of thousands) and p (several hundreds), the number of equations is large and the calculations become very CPU time and memory consuming. This difficulty can be solved for very large values of n, by using, for instance the Fokker–Planck formalism and casting the rate equations with n replaced by a continuous variable x for large values of n.

Note that another family of mesoscopic scale method, phase field methods which were developed twenty years ago is also now been applied in radiation damage modelling to investigate the evolution of the nanoscale features formed under irradiation.

3.3 Dislocation dynamics – from the experimentally resolvable defects to the yield stress

Plasticity is controlled by the motion of dislocations and their interaction with the objects present in the materials. Usually, dislocation properties and interactions are investigated on two phenomenological scales, the atomic and the continuum (mesoscopic) levels. Atomic simulations using first principles and MD techniques are used for a direct investigation of

dislocations, taking into account the dislocation core structure and its related thermally activated processes. Dislocation dynamics (DD) simulations are then used to study dislocation properties and their collective behaviour including mobility, dislocation–dislocation interactions and dislocation-irradiation defect interactions at different temperatures. Dislocation core structures can be investigated using first principles calculations which can help validate the empirical potentials used to model dislocation motion in the presence of irradiation defects and obtain the critical stress. Note that the critical stress as a function of the applied shear deformation to move a single screw dislocation, cannot be used directly as an input parameter for DD modelling or directly compared to experimental results, because the experimental deformation rates are much lower than the deformation rates that can be modelled within MD and the typical distances too large (they typically correspond to grain sizes of the order of the μm). Consequently scaling relation laws, based, for instance on the physical thermally activated processes involved, have to be elaborated in order to interpret the atomic simulation results.
Furthermore, standard interpretation of experimental results and mesoscale simulations assume quasi-static conditions, whereas, the MD simulations cannot be considered as quasi-static. As a result, the time dependency of the dislocation motion and the dislocation-defect interaction induced by the thermal activation of the physical processes have to be taken into account using specific thermodynamical analysis methods.

3.4 First principle calculations

First principle calculations are techniques used to obtain atomic and molecular structures directly from the first principles of quantum mechanics, i.e. without using quantities derived from experiment as parameters. They require a large amount of numerical computation as the amount of computing time increases rapidly as the size of the supercell, i.e. the number of atoms or molecules increases. The common objective of all the ab initio techniques is to solve for the Hamiltonian of a system containing N_a atoms and N_e electrons. This is a many body problem which can only be solved with a certain number of approximations. The first one being the Born Oppenheimer approximation or adiabatic approximation which allows to treat the electrons as moving in the potential generated by motionless nuclei, owing to the fact that the mass difference between the nuclei and the electrons is at least three orders of magnitude.
In the field of materials science, first principle calculations are based on the Density Functional Theory (DFT) which states that the ground state energy of a many-electron system can be expressed as a unique function of the electron density. The DFT has its conceptual roots in the Thomas-Fermi model, but it was put on a firm theoretical footing by Hohenberg and Kohn and Kohn and Sham in the mid 60's. One of the important approximation in DFT concerns the exchange and correlation. The most simple one and the most widely used, the Local Density Approximation (LDA), considers the exchange and correlation energy to be the same as an homogeneous electron gas with the same density. Behind LDA, the Generalised Gradient Approximation (GGA) takes into account in addition the gradient of the density. Strongly correlated systems, encountered with some rare earth elements (with localised f orbitals) or some insulating transition-metal oxides (predicted to be metals within the LDA, e.g. NiO, UO_2) are among the most difficult elements to describe, and are not well described by standard DFT formalisms based on LDA and GGA. Recent developments such as LDA + U, hybrid functionals, or GW methods lead to an improvement of the modelling of the electronic properties and allow better predictions.

From a numerical point of view, an issue that has to be taken into account is that the computing cost of first principles methods is not linear with the system size (i.e. the number of electrons), mainly because of linear algebra calculations on some dense matrixes. Some developments and research works are ongoing in order to search for linear scaling methods. The search of linear scaling method is quite complex and there is no general solution for any kind of system (molecular, lamellar or bulk structures) and/or materials (metal, semi-conductor, insulator). Low dimension systems (e.g. molecules) and insulators are the easiest case for linear scaling as locality of the interaction with a localised basis set lead to sparse matrices for which fast linear algebra algorithms can be applied.

At the moment DFT calculations are limited to few hundreds of atoms, on massively parallel computers. Many DFT codes are now available which differ by

- the local basis sets which are used to pave the space. In metals, plane waves, because of their simplicity are very often used, but localised orbitals are also found in some codes.
- the number of electrons which are explicitly taken into account. To simulate large systems, one usually considers that the core electrons are frozen. These kind of simulations are less computationally demanding than the so-called "all electron" methods such as the Linearized Augmented Plane Wave (LAPW) method. In the former case, the inner core electrons are modelled using pseudo potentials or more sophisticated techniques such as Projector Augmented Wave .
- the method to reach the ground state

To perform first principles MD, one can use the classical Born Oppenheimer approximation wherein the nuclear degrees of freedom are propagated using ionic forces which are calculated at each iteration by approximately solving the electronic problem with conventional matrix diagonalization methods, or the Car–Parrinello approach which explicitly introduces the electronic degrees of freedom as (fictitious) dynamical variables, writing an extended Lagrangian for the system which leads to a system of coupled equations of motion for both ions and electrons.

DFT calculations are commonly used nowadays to determine the properties of point defects and their clusters as well as to investigate the behaviour of foreign interstitial atoms (e.g. C, N in Fe) and solute atoms (e.g. Cu, Ni, Mn, Si, P in Fe) (**Fig. 5**).
The data obtained are used in the assessment of empirical interatomic potentials and for the development of new potentials. In the field of radiation damage, interatomic potentials used for years to simulate α-Fe were called into question when DFT calculations showed that the rotation energy from the ⟨110⟩ to the ⟨111⟩ SIA configuration might be higher than 0.7 eV (to be compared to the close to 0.1 eV predicted by empirical many-body potentials used at that time), and have predicted a migration energy of 0.34 eV in agreement with the experimental results. Consequently, some empirical potentials have been refitted including DFT results in the database.

Figure 5: typical results obtained using DFT calculations ⟨110⟩ SIA configuration and the local magnetic moments carried by the atoms in bcc Fe. Carbon-carbon covalent bond interaction (red atoms) within a single vacancy (white square)

Another use of first principle calculations in the multi-scale approach can be found in the KMC modelling. The key ingredient of the KMC models, which guarantees the correct modelling of a given system and of its kinetic pathways is the description of the diffusion mechanisms and rates. The activation energies can be obtained using cut-bond models, energy difference for the transition considered, or neural networks guesses trained on limited sets of saddle point energy calculations. The system energies can be determined using interatomic potentials when they exist, which at the present time is true only for simple binary or ternary alloys. For more complex alloys, for which no interatomic potentials exist, one has to resort to use neighbour pair interactions which can be fitted on DFT results.

4. VALIDATIONS OF THE MODELS

Finally, before going on a "materials behaviour" prediction mode with confidence, it is necessary to compare the predictions of the data with experimental results and in multi-scale approach, this needs to be done for each sub-module. The most difficult part is the experimental measurement of physical quantities at the atomic scale. Fortunately, in parallel to the increase of the computation powers, the accuracy of the experimental techniques has made large progress. Experimental techniques carefully chosen allow to analyse one type of defect on a range of detectable sizes; thus the use of different techniques on the same material specimen provides a better picture of the microstructure. The advanced techniques used nowadays are the tomographic atom probe to have the solute distributions, positron annihilation spectroscopy which provide information on vacancies and voids, transmission electron microscopy to quantify dislocation loops and voids larger than few nanometers, small angle neutron scattering to analyse solute-defect clusters.
The comparison between the experimental data and the models is never straightforward as for instance, the experimental signal has to be interpreted using models which rely on the knowledge one has of the physics involved. Furthermore, "simulated materials" are perfect in contrast with real materials. Many of the experiments available nowadays were made 30 or 40 years ago. Since then, the influence of impurities, even in very residual amount, has been pointed out, and one research direction that needs to be pursued to characterise more properly the interactions between point defects and solute atoms is the setting up of new sets of simple experiments, such as the recovery experiments, on materials with the highest purity possible in order to eliminate unwanted effects, as well as experiments on model alloys with increasing chemical complexity to validate the models developed.
To progress in this field, one needs to design dedicated experiments in a close collaboration between experimentalists and modellers. The goal is to perform experiments on models alloys with the same number of elements that simulation can currently safely take into account (and some inevitable impurities) and also with simplified irradiation conditions (electrons irradiations, simple or joint ion irradiation, before treating neutron irradiation)
Both experimentalists and modellers benefit from this type of collaboration, because it gives access to experimental conditions where the numerous possible interactions defects, elements, and microstructure features have been decorelated

from one another (compared to the complex industrial multicomponent case), which makes it possible to test one by one the experimental and numerical models describing these interactions.

5. CONCLUSIONS

Multiscale modelling is now commonly developed to simulate radiation damage in structural materials of nuclear power plants. It is based on elementary atomic mechanisms and takes into account both point defects, the chemical composition of the alloys (e.g. some of the solute most important species), and their interaction at the atomic scale which affect the microstructure evolution and consequently the usage properties. The use of a collaborative approach involving experiments, theories and modelling is, to our point of view, the most promising way to understand the many aspects of the solute point defect interactions and their consequences on the evolution of the microstructure.

REFERENCES

Books and book chapters:

Simulations at the atomistic level

-"Computer Simulations of Liquids", M.P.Allen and D.J. Tildesley, Clarendon Press., Oxford, (1987)

-"Understanding Molecular Simulation ", D. Frenkel and B. Smit, Academic Press, San Diego, London, Boston, New York, Sydney, Tokyo, Toronto (1996)

First principles calculations

-"Electronic structure: Basic Theory and Practical Methods", Richard M. Martin, Cambridge University press, (2004)

Multiscale modeling of nuclear materials

-"Understanding and mitigating ageing in nuclear power plants", Ph.G. Tipping ed., Woodhead Publishing Ltd. (2010), Chapter 15 by L. Malerba.

-« Basic Aspects of Radiation Effects in Solids/Basic Aspects of Multi-Scale Modeling », Volume 1 of Comprehensive Nuclear Materials, Elsevier, 2012.

Dislocations and dislocation dynamics

-" Computer Simulations of Dislocations" Bulatov V. and Cai W., Oxford Series on Materials Modelling 3; Clarendon Press, Oxford, (2006).

Articles

Empirical models:

-"25 years of Finnis-Sinclair potentials and related issues", special issue of Phil. Mag, vol. 89 (2009).

Multiscale modeling of nuclear materials

-"FP6 IP PERFECT Project: Prediction of Irradiation Damage Effects in Reactor Components", special issue of *J. Nucl. Mater*. vol. **406** (2010)

- Becquart C.S. and Domain C., "Modeling Microstructure and Irradiation Effects »*Metal. Mater. Trans. A* **42** (2011) pp.852-870.

Obtaining the neutron and PKA spectrum

SPECTER: Greenwood L. R., Smither R. K.: "SPECTER: Neutron Damage Calculations for Materials Irradiations", ANL/FPP-TM-197 Report, Argonne NL, January 1985; code available at: http://www.nea.fr/abs/html/psr-0263.html; see also Greenwood L. R., *J. Nucl. Mater*., 1994, vol. 216, pp. 29-44.

DART: Lunéville L., Simeone D. and Jouanne C.: *Nucl. Inst. Meth. Phys. Res. B*, 2006, vol. 250, pp. 71-75.

Lunéville L., Simeone D. and Jouanne C.: *J. Nucl. Mater.*, 2006, vol. 353, pp. 89-100.

Molecular Dynamics codes

LAMMPS (Large-scale Atomic/Molecular Massively Parallel Simulator): http://lammps.sandia.gov/

XMD : http://xmd.sourceforge.net/

DYMOKA : Becquart C.S., Decker K.M., Domain C., Ruste J., Souffez Y., Turbatte J.C. and Van Duysen J.C.: *Rad. Eff. Def. Sol.,* **142** (1997) pp. 9-21

MOLDY: Finnis M. W., "MOLDY6-A Molecular Dynamics Program for Simulation of Pure Metals," AERE R-13182, UK AEA Harwell Laboratory (1988); Calder A. F. and Bacon D. J.: *J. Nucl. Mater*., **207 (**1993) pp. 25-45.
MDCASK: Soneda N. and Diaz de la Rubia T.: *Phil. Mag. A*, **78** (1998), vol., pp. 995-1019
DLPOLY: http://www.cse.scitech.ac.uk/ccg/software/DL_POLY/

KMC and MFRT

- Fichthorn K.A., Weinberg W.H., "Theoretical foundations of dynamical Monte Carlo simulations", *J. Chem. Phys*. **95** (1991) pp.1090-1096
- Johnson R.A., "Kinetic study of vacancy clustering and annealing in metals", *Phys. Rev.,* **174** (1968) vol. 174, pp. 684-690.
- Brailsford A.D. and Bullough R.: *Phil. Trans. R. Soc. London*, **302** (1981) pp. 87-, and references therein.
- Becquart C.S. and Domain C., "Introducing chemistry in atomistic kinetic Monte Carlo simulations of Fe alloys under irradiation", *Phys. Stat. Sol.* **247** (2010) pp.9-22.
- Stoller R. E., Golubov S. I., Domain C. and Becquart C. S., "Mean field rate theory and object kinetic Monte Carlo: A comparison of kinetic models", *J. Nucl. Mater*., **382** (2008) pp.77-90.

Dislocations and dislocation dynamics

- Foreman A.J.E. and Makin M.J., "Dislocation movement through random arrays of obstacles", *Phil. Mag*., **14** (1966), pp 911-924.
- Devincre B. and Condat M. "Model validation of a 3D simulation of dislocation dynamics: Discretization and line tension effects", *Acta Metall. et Mater*., **40** (1992) pp.2629-2637.
- Roberts S. G., Ellis M. and Hirsch P. B. "Dislocation dynamics and brittle-to-ductile transitions", *Mater. Science and Eng. A*, **164** (1993) pp.135-140.
- Zbib H. M., de la Rubia T. D., Rhee M and Hirth J.P., 3D dislocation dynamics: Stress-strain behavior and hardening mechanisms in fcc and bcc metals", *J. Nucl. Mater*., **276** (2000) pp.154-165.

Phase field methods

-Boettinger W. J., Warren J. A., Beckermann C., Karma A. "Phase-field simulation of solidification", *Annu. Rev. Mater. Res.* **32** (2002) pp.163–194.
-Chen L.-Q. "Phase-field models for microstructure evolution", *Annu. Rev. Mater. Res*. **32** (2002) pp 113–140.
-Thuinet L., De Backer A., Legris A., "Phase-field modeling of precipitates evolution dynamics in elastically inhomogeneous low-symmetry systems: application to hydride precipitation in Zr", *Acta Mater.,* **60** (2012) pp.5311-5321.