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# Molecular dynamics simulation of defect formation in irradiated Ni

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We present here the results of molecular dynamics simulations of collision cascades in nickel irradiated with 500 eV ions, with the aim of studying the degradation of the physical properties of face centered cubic (fcc) metallic materials used in nuclear power plants. We simulated a system of 13 500 atoms (a lattice of $30 \times 30 \times 15$) using periodic boundary conditions only along the transverse directions, perpendicular to the direction of the initial impact. We kept the system at constant temperature and performed multiple runs, changing slightly and randomly the direction of the projectile ion. Simulations for up to 5 ps showed that the total number of defects has a sharp increase up to a maximum at about 300 fs, followed by a relatively fast decrease. During the time of the simulation, the various numbers of vacancies (we analyzed di-, tri-, tetra- and multiple vacancies) grow sharply in the beginning and than, after about 300 fs, decrease, indicating that the vacancy clusters break apart into smaller clasters and simple vacancies. Although during the collision cascade some regions of the sample become amorphous, due to local melting, during the relaxation phase most of the displaced atoms return to equilibrium positions, causing recrystallization.

## 1. Introduction

The study of the irradiation-induced defect formation in various metals and metal alloys is of interest in order to understand the degradation of the physical properties of the materials used in pressure vessels in nuclear power plants as well as in metal coatings for fusion-based alternative energy sources [1, 2]. Most damage

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produced in materials during ion irradiation derives from complex processes occurring in collision cascades [3].

While collision cascades produce defects in a region of the order of nanometers and on a time scale of tens of picoseconds, being easily modeled by molecular dynamics (MD), defect migration and diffusion occurs over longer time scales, of the order of nanoseconds and milliseconds, or larger, respectively, and can be simulated by kinetic Monte Carlo; even further, the changes in the microstructure can be studied by finite element methods and imply time scales of the order of seconds or larger [4].

Irradiation of materials by high-energy ions produces Frenkel pair defects, which are interstitial-vacancy pairs. The migration of these individual defects leads to either their recombination or to the formation of vacancy or interstitial clusters [4]. Recently, a study of the defect kinetics in irradiated iron showed that the barriers to migration of multiple vacancies are low, suggesting that the vacancies can move through the solid in clusters of various sizes [5].

In this article we study the production of Frenkel pair defects during the collision cascades produced by a recoil atom with the initial kinetic energy of 500 eV in a target of 13500 Ni atoms. We study the time evolution of the resulting vacancies as well as their migration towards the surface. We find that the metal suffers local melting and that the thermal spike phase lasts up to a 400 fs. The metal then recrystallizes leaving behind only a small number of defects in the bulk.

## 2. Model and principles of the simulation

In molecular dynamics simulations the time evolution of a system of atoms is calculated by solving the equations of motion numerically [6]. The molecular dynamics simulation process starts by calculating the force acting on each atom in the system. The equations of motion for the system are solved using some suitable algorithm [6, 7]. The solution yields the change in the atom positions, velocities and accelerations over a finite time step $\Delta t$. After the atoms have been moved the simulation continues by recalculating the forces in the new positions. The atoms that are included in the calculation are usually placed in an face-centered cubic lattice within an orthogonal simulation cell.

The forces governing the simulation can be obtained from classical or quantum mechanical calculations. Although promising advances have recently been made using tight-binding molecular dynamics methods, quantum molecular dynamics methods are still far too time-consuming to allow simulation of full collision cascades [8]. Therefore classical MD simulations have to be used in the foreseeable future for descriptions of energetic collision cascades.

In classical MD simulations the interaction between atoms in the sample are described with an interatomic potential $V(r)$, generally assumed to depend only on the distance $r$ between two atoms. One of the most common choices for the interatomic potential, asside from the Lennard-Jones potential, describing closed shell systems such as the noble gases, is the Morse potential [9], more suitable for cubic metals [10].

The expression of the Morse potential is given by:

$$V_M(r) = D\big[\mathrm{e}^{2\alpha(r-r_e)} - 2\mathrm{e}^{\alpha(r-r_e)}\big], \tag{1}$$

whre $r$ is the distance between the atoms $r_e$ is the equilibrium bond distance, $D$ is the depth of the potential energy well, and $\alpha$ controls the width of the potential. For nickel the values of these constants are: $D = 0.4205\,\mathrm{eV}$, $\alpha = 1.4199\,\mathring{A}^{-1}$, $r_e = 2.780\,\mathring{A}$ [10].

In molecular dynamics simulations the time evolution of a system of atoms is calculated by solving the equations of motion numerically. In the Newtonian formalism the force acting on an atom is calculated based on the sum of the contributions of all other particles, taking into account the gradient of the interatomic potential [6]. After the force calculation, the equations of motion for the system are solved using an integration algorithm, to provide the new positions and velocities for each particle at the next moment. The time step, $\Delta t$, is appropriately chosen to optimize a compromise between accuracy and duration of the simulation. The process is repeated by calculating the forces in the new positions and integrating to find the new positions and velocities.

Our simulation algorithm is based on Newtons classical laws of motion. The most common integration algorithm is the so called velocity Verlet algorithm [11], whose defining relations are:

$$\mathbf{r}(t+\Delta t) = \mathbf{r}(t) + \mathbf{v}(t)\Delta t + \mathbf{a}(t)(\Delta t)^2/2 \tag{2}$$

$$\mathbf{v}(t+\Delta t) = \mathbf{v}(t) + [\mathbf{a}(t) + \mathbf{a}(t+\Delta t)](\Delta t)/2 \tag{3}$$

The positions and velocities at a given moment are determined based on the positions and velocities at the previous moment and the accelerations at both the previous and the present time.

In more sophisticated simulations at constant temperature and pressure, the equations of motion are more complicated, originating, however, from the same Newtons law. The temperature and the pressure of the system are kept constant for instance by scaling the velocities and positions of all the particles, respectively, following a certain equilibration time frame. A typical approach is the one proposed by Berendsen [13], which introduces the scaling factor

$$\lambda = \sqrt{1 + \frac{\Delta t}{\tau_T}\Big(\frac{T_d}{T} - 1\Big)} \tag{4}$$

where the temperature equilibration time ($\tau_T$) is, usually, $\tau_T > 100\Delta t$. Here, $T_d$ is the desired temperature.

The infinite range of the potential implies that every particle interacts with all the other. As the simulated systems grow larger and larger the number of force computations grows with the square of the number of particles, leading to long computer times for each run. A partial solution to this problem is the potential truncation, suggested by the rapid decrease of the strength of the interaction at large distances [6]. The typical cutoff radius for the Morse potential is $r_c = 1.8r_e$.

The initial energy was chosen at 500 eV, based on two main competing criteria. First, sufficient energy is needed to cause major collision cascades, relevant to describe the defect generation and the time evolution of the vacancies. Statistical relevance can be obtained if more than only a few vacancies (say 20 such vacancies) are produced in one recoil event [14]. Secondly, the energy had to be small enough to prevent the complete passage through the target. The passage through the target can be prevented if the system has 25-40 atoms for each eV of the incoming ion [1]. Constraints related to the time and computer power available lead to the choice of a system of 13 500 atoms ($30 \times 30 \times 15$ atomic layers).

As the number of particles used in the simulations is relatively small a real system can be simulated only using periodic boundary conditions [6]. The boundary conditions apply only along the two transverse directions with respect to the incoming ion and insure that i) once a particle escapes through a wall it has to enter the system from the opposite side, and ii) when distances between particles are evaluated, one has to choose between the particle or its image in the adjacent box to determine the total force on the respective particle.

The time step $\Delta t$ is usually fixed in simulations of systems in thermal equilibrium. In collision cascade calculations the initial time step must be very short. Therefore, using a fixed time throughout the simulation is very ineffective. Instead, we choose the length of the time step dynamically to allow a good compromise between the speed and the accuracy of the simulation. At the beginning of the collision cascade the time step is made inversely proportional to the velocity of the fastest moving atom. The time step becomes longer as the recoil atom slows down, significantly reducing the calculation time. After the collisional phase the time step is held constant again, equal to 2 fs.

The initial state of the system was prepared by equilibrating 13 500 nickel atoms located on a fcc crystalline lattice. In the initial displacement calculation, periodic boundary conditions and a constant time step of 2 fs are used. The atoms are given initial velocities in random directions following a Maxwell distribution corresponding to a given initial temperature. The final (desired) temperature was set for 300 K. The simulation is carried out until the average temperature averaged over the last 2 000 time steps yields the desired temperature T (within the error bounds).

During the preparation of the equilibrium state the pressure of the system was also monitored [15, 16]. The cell size is scaled such that the system returns to atmospheric pressure, as during the first steps of the equilibration process it departs from the initial value of atmospheric pressure.

The simulations were performed on a personal computer with an Intel Dual Core processor running at 3.0 GHz clock speed, using an in house program written in C based on the MDRANGE program [17].

## 3. Results and discussion

The time evolution of one of the collision cascade events simulated is shown, using RasMol [18], in Fig. 3. The grayscale coding shown in the inset of Fig. 3, is a

logarithmic scale representing the kinetic energy of the particle, with ranges from high energies (dark grey) to room temperature energies (light grey). The damaging effects of the collision are spectacular, as the energy of the incoming particle is transferred to the target atoms, causing major defect formation. It can be seen that the projectile follows a straight path until 150 fs, when colisions determine secondary recoil particles to move outwards. The collision phase is followed by the thermal spike phase, which allows for heat dissipation. At 400 fs the shock wave is almost spherical with many atoms in the impact region displaced from their equilibrium positions, indicating the local melting of the target. The melting indicates heat dissipation from the projectile and secondary recoil particles to the solid. At 700 fs the atoms have already released a large part of their energy and started to relocate, the melted region being about to recrystallize. The thermal spike phase ends before 700 fs, being followed by the relaxation phase. As time passes the atoms tend to occupy ordered position in the lattice and the target recrystallizes.

Moving from the representation of the atoms involved in the collision cascade to that of the defects generated in the collision event shown in Fig. 3, we display in Fig. 4 the time evolution of all the vacancies. It can be seen that at the beginning of the collision phase the vacancies are preponderantly produced along the main recoil direction (100 fs) and in a small number on the secondary recoil directions (150 fs). As time passes, the defects spread in the bulk being produced in clusters in the volume of the sample (250 fs), in the melted region. After 400 fs the total number of vacancies decreases. The defect clusters break into smaller clusters, increasing the number of monovacancies. Some of the vacancies remain trapped in the bulk even after 3000 fs, surviving even the slow relaxation phase that follows. Our results are in agreement with the description of migration of vacancies and interstitials of Nordlund and Averback [14]. The results of ten individual collision events and the average calculated from them are show in Fig. 1. It can be seen that during the first 200 fs the number of vacancies rises almost equally abruptly for all the events but afterwards fluctuations occur. The maximum number of vacancies is reached at about 300 fs, which confirms the qualitative conclusions drawn from Figs. 3 and 4. After 1000 fs, in the relaxation phase, the number of vacancies decreases slowly. The total number of vacancies that remain after 3000 fs, about 5, is in good agreement with the number of vacancies predicted by the Kinchin-Pease relation. This result is in contrast with our previous observations for Cu [15, 16]. The time evolution of the various numbers of vacancies is shown in Fig. 2. All types of vacancies (mono-, di-, tri-, and tetra-vacancies) increase very fast at the beginning of the cascade, but decrease slowly after that. The time evolution of the various types of multiple vacancies indicates that the defect clusters tend to break into smaller pieces during the recrystallization process, in agreement with the images in Fig.4.

## 4. Conclusions

We used molecular dynamics simulations to describe the radiation-induced defect formation in nickel. We studied collision cascades and the time evolution of the

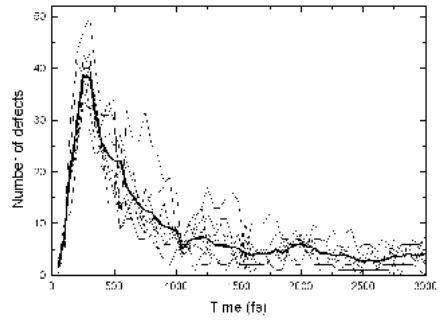


Fig. 1. Time evolution of the number of vacancies produced by 500 eV recoils with randomly selected initial recoil direction. Ten individual events and the average calculated from them are shown.

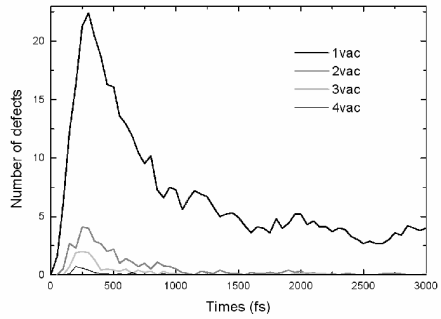


Fig. 2. Time evolution of the number of mono-, di-, tri- and tetra-vacancies. The values presented are averages calculated over 10 events.

complex vacancies produced by ion irradiation of metallic targets. We found that the number of vacancies increases abruptly in the collision phase, reaches a maximum at about 300 fs and decreases slowly afterwards. During the relaxation phase, the melted regions tend to recrystallize. The vacancy clusters break apart, increasing the numbers of single vacancies, which, in turn are filled with interstitial atoms which find equilibrium positions within the lattice. We found that for nickel, after 3000 fs, the total number of vacancies is in good agreement with the one predicted by the Kinchin-Pease equation, unlike our previous results for copper. We concluded that, with a lower number of surface defects, Ni reaches much faster than Cu also the bulk recrystallization.

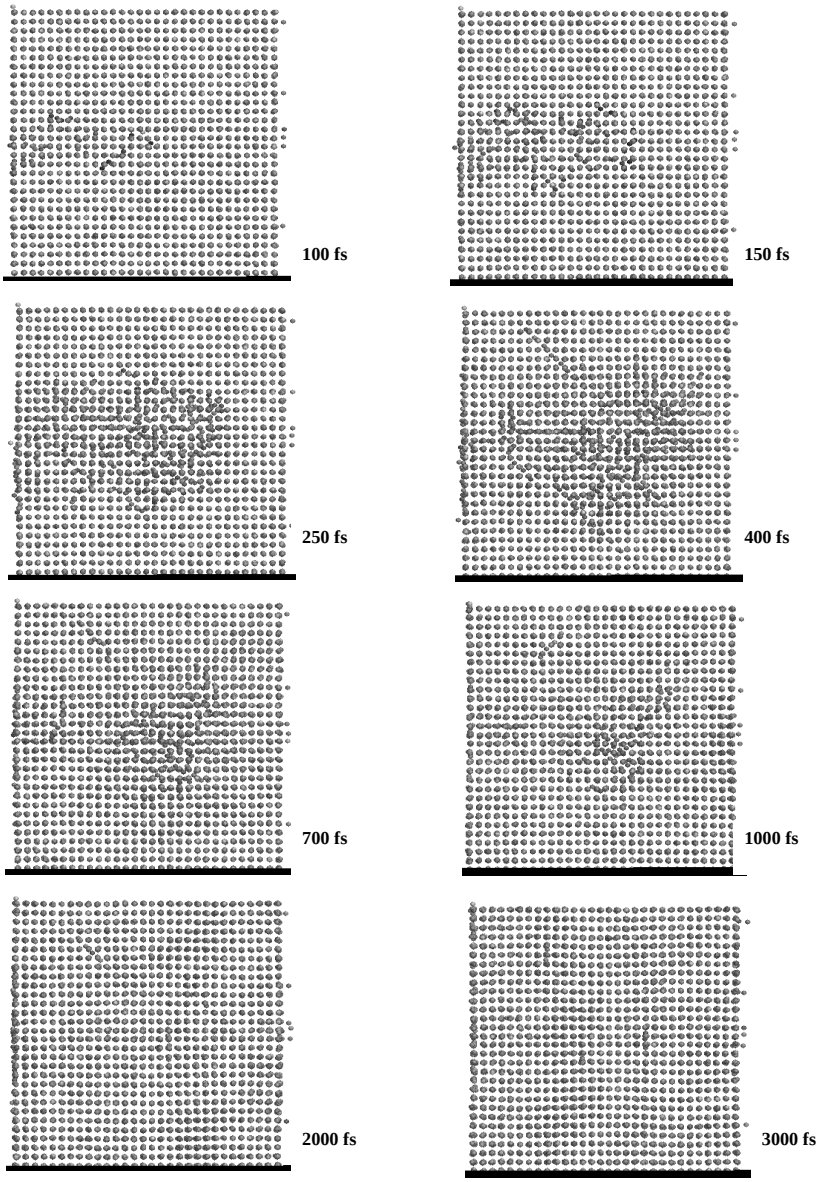


Fig. 3. Lateral view of a 500 eV collision cascade in Ni at various times. Inset: The greyscale energy coding: From left to right, the kinetic energy is: $< 0.005$ eV, 0.005-0.03 eV, 0.03-0.06 eV, 0.06-0.10 eV, 0.10-0.14 eV, 0.14-0.20 eV, 0.20-0.35 eV, 0.35-0.50 eV, 0.5-0.7 eV, 0.7-1.2 eV, 1.2-5 eV, 5-25 eV, $> 25$ eV.

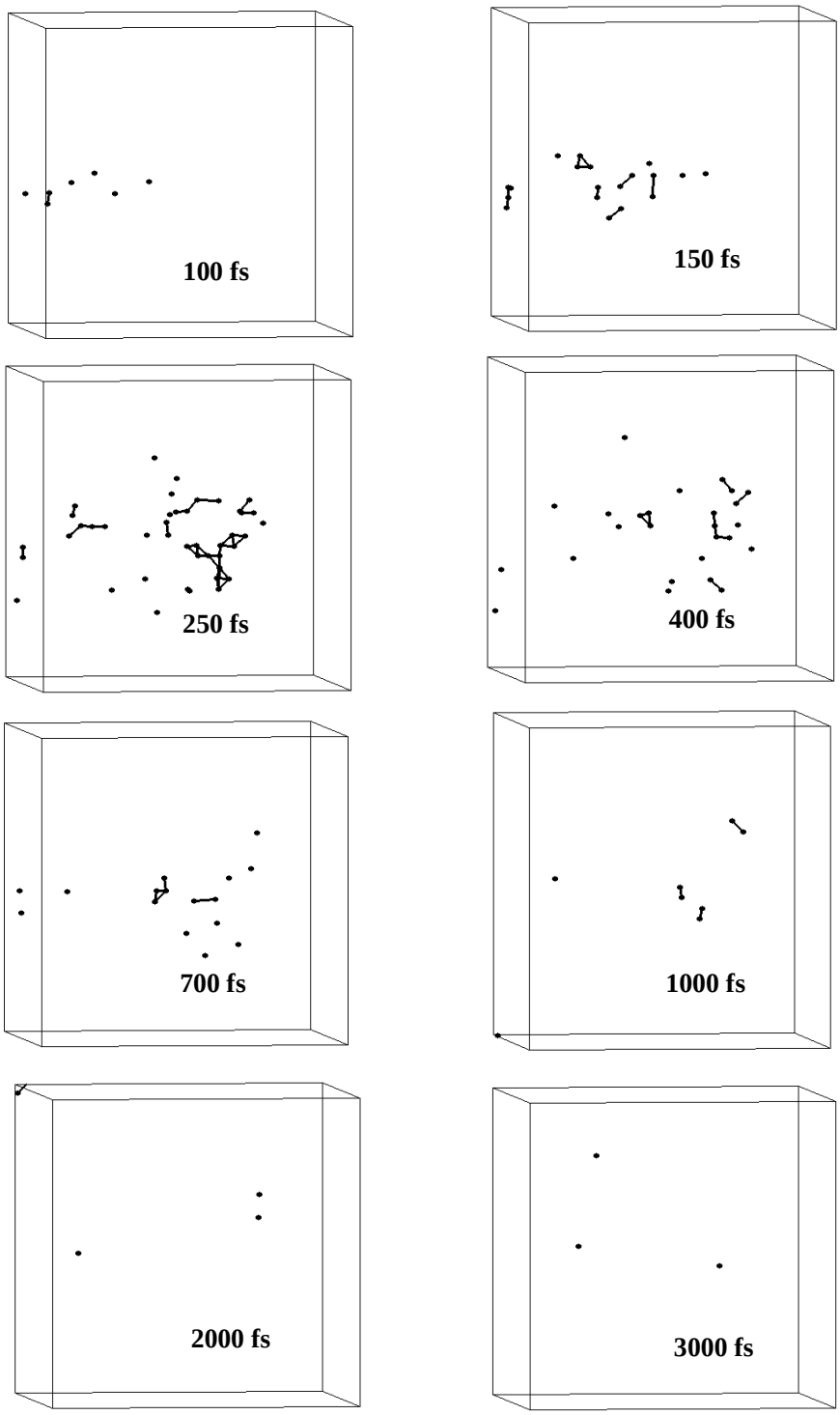


Fig. 4. The time evolution of all vacancies formed in the collision event displayed in Fig. 1. The vacancies are represented with dots and, in the case of vacancy clusters, they are connected with lines.

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