

Energy evolution in nanocrystalline iron driven by collision cascades

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Abstract

Nanocrystalline materials are promising candidates for future fusion reactor applications, due to their high density of grain boundaries which may serve as sinks for irradiation induced defects. We use molecular dynamics to simulate collision cascades in nanocrystalline iron and compare these to collision cascades in initially defect free single crystals. We create nanocrystalline samples via Voronoi tessellation of initially randomly placed grain seeds and via severe plastic shearing. An irradiation induced annealing is observed whereby after ~ 2 displacements per atom (dpa), irradiation drives all simulation cells to a single crystalline state. Irradiation-induced defects that distort the lattice generate elastic strain, so we use excess potential energy as a measure of defect content. At low doses, the Voronoi samples feature a few large, low energy grains, whereas the sheared samples show many small, high energy grains due to the high defect and grain boundary content caused by severe deformation. As dose increases beyond 1 dpa however, all nanocrystalline samples converge to a similar behaviour. Excess potential energy mirrors this trend, plateauing above ~ 4 dpa. We hypothesise that the initially pristine cells will also reach a similar plateau after 5 dpa, which is seemingly confirmed by running a single instance of each cell type to 10 dpa. A model is developed to explain the energy evolution.

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We conclude that, regardless of initial structure, irradiation drives all cells toward the same energy state at high doses.

Keywords: Nanocrystalline iron, Collision cascades, Energy evolution

1. Introduction

High-energy neutrons are the main product of the deuterium-tritium nuclear fusion reaction [1]. In operation, these neutrons will penetrate the reactor materials, interacting with the atomic nuclei. These interactions produce atomic recoils [2], which create collision cascades within the material leading to the production of dislocations, voids, and other microstructural defects. These defects cause a degradation of the reactor materials' mechanical [3, 4, 5] and thermal [6, 7] properties.

Nanocrystalline materials have been considered for use in fusion applications [8] due to their high grain boundary density, which may act as a sink for irradiation induced defects [9, 10, 11, 12]. These materials are characterised by their small grain size (< 100 nm), and experimentally, a lower irradiation defect density has been observed for nanocrystalline materials when compared to coarse-grained material irradiated to the same dose [13, 14].

Experimental techniques such as high-pressure-torsion, accumulative roll bonding, and equal channel angular pressing, have been extensively used to produce nanocrystalline materials through severe plastic deformation (SPD) [15, 16, 17, 18, 19]. Traditionally, molecular dynamics (MD) studies on nanocrystalline material have used Voronoi tessellation [20] with randomly placed grain seeds to generate nanograined simulation cells. Recently, studies have been carried out on the creation of nanocrystalline materials in MD through SPD [21, 22]. Tolkachev *et al.* [21] induced grain refinement in iron by applying a high shear strain (up to $\gamma = 10$) to initially pristine simulation cells. Nanograin formation was directly observed and the grains were found to be stable at constant temperatures of 300 K, 500 K, and 800 K, for 1 ns.

Irradiation induced annealing processes have been observed in materials both experimentally [5, 13, 23, 24, 25] and through MD simulations [26, 27, 28]. Song *et al.* [5] irradiated nanocrystalline and coarse-grained Eurofer97 with self-ions. An irradiation induced annealing process was revealed through X-ray diffraction measurements which showed grain coarsening and a reduction of dislocation density with increasing irradiation dose. Ma *et al.* [26] used MD simulations to study irradiation damage in nanocrystalline

tungsten by utilising the creation relaxation algorithm [29]. Similarly to the experimental findings, a grain coarsening occurred with increasing dose. Levo *et al.* [27] also observed irradiation induced grain growth in nanocrystalline nickel subjected to collision cascade simulations. Tolkachev *et al.* [28] reported a grain coarsening with irradiation in nanocrystalline iron. This combined atomistic and experimental study also confirmed grain coarsening in self ion-irradiated, nanocrystalline iron discs, and the MD data suggested a linear grain growth, which was consistent with the experimental values.

Every grain within a material will have inherent elastic energy due to the elastic strain field associated with grain boundaries and crystal defects. It is expected that the irradiation induced annealing process reported both in experiments [5, 13, 23, 24, 25] and MD simulations [26, 27] will reduce the elastic energy, as grain growth and annealing occurs. The potential energy will be a sum of defect formation energy, grain boundary energy, and elastic energy. As such, tracking the excess potential energy as a function of irradiation is a useful method of measuring the integrated effect of grain growth and defect reduction for initially nanocrystalline MD simulation cells.

Reduced activation ferritic/martensitic (RAFM) steels such as Eurofer97 and T91 are promising candidate materials for future nuclear fusion reactors. Previous studies have explored their irradiation resistance [30, 31, 32, 33], and Garner *et al.* [30] reported that RAFM steels with body-centred-cubic structure, were more resistant to irradiation induced swelling than austenitic steels. RAFM steels are iron-based alloys and in this work, we use iron (Fe) as a prototypical material to gain mechanistic insight into its evolution under irradiation.

An established method for simulating irradiation damage using MD simulations is through collision cascades [27, 34, 35, 36, 37]. This method selects random atoms in a simulation cell and assigns velocity in a random direction corresponding to an expected primary-knock-on atom (PKA) energy.

In this work, nanocrystalline iron cells created through Voronoi tessellation [20] and through the shearing method reported by Tolkachev *et al.* [21] are considered. These cells are subjected to irradiation through collision cascade simulations and the evolution of excess potential energy within the cells is tracked as a function of dose. First, the excess potential energy is calculated for all cells and compared. Then, the excess potential energy is calculated for each individual grain for different types of starting microstructure. This gives insight into how grains evolve during irradiation. Finally, the implication of these results is discussed before drawing conclusions.

2. Methods

2.1. Simulation Setup

LAMMPS was used for all MD simulations [38] in this work. Two distinct methods were employed to generate nanocrystalline iron cells; Voronoi tessellation [20] and the high shear strain method proposed by Tolkachev *et al.*[21], hereby denoted as the *sheared* cells. In the case of the Voronoi cells, two different grain numbers were seeded for comparison: one with 5 grains per cell ($d_c = 16.6$ nm) and the other with 20 grains per cell ($d_c = 5.2$ nm). The diameters are calculated using the spherical grain approximation. Five independent cells are created for each initial condition, and the results and errors below are calculated with respect to five simulations for each type of microstructure. For comparison, five additional initially pristine iron cells were also irradiated through collision cascades.

All cells contained 1,024,000 atoms which corresponds to $80 \times 80 \times 80$ unit cells of BCC iron. The cell relaxation method reported by Ma *et al.*[26] was followed for all distinct simulation cells. An extra step was added to the sheared cells in that they were initially thermalised to 300 K and sheared up to $\gamma = 10$. By utilising the method in [26], the cells achieved stress free conditions and were brought down to a temperature of 0 K before the collision cascade simulations. The dataset considered here was also used in Tolkachev *et al.* [28]. Previously, Tolkachev *et al.* determined that the Voronoi cells' grain volume correlated well to the equation of Ference *et al.* [39], whilst the grain volume distribution of the sheared cells was fit to a Zipf-Mandelbrot model [40].

The potential used in this study is the Mendelev *et al.*[41] Fe2 potential. This belongs to the Ackland-Mendelev family of iron potentials which have been used extensively for the study of irradiation damage effects in iron and iron alloys [36, 29, 42, 43, 44]. Indeed, Malerba *et al.* [44] commented that the Mendelev-type potentials are the best choice for studying irradiation effects on iron when compared to density functional theory.

Collision cascade simulations were employed to replicate neutron damage in the nanocrystalline iron. The method in Tolkachev *et al.* [28] was followed which is based on the collision cascade method developed by Boleiningner *et al.* [34]. The Stopping and Range of Ions in Matter (SRIM) [45] code was used to determine the recoil energies of primary knock on (PKA) atoms in iron. These recoil energies were then sampled from for each collision cascade simulation to ensure a target dose was obtained in each step. Appendix A of

Tolkachev *et al.* [28] shows the recoil energy distribution that was sampled in this work. It is dominated by lower energy recoils (30 - 200 eV), with a much lower probability of selecting higher energy recoils (200 eV - 20 keV). The exclusion radius of each PKA is also calculated to ensure there is no overlap between cascades.

Each distinct simulation cell was irradiated to 5 dpa, with a single instance of each cell type being irradiated to 10 dpa through collision cascade simulations. Each primary-knock-on (PKA) atom energy was converted to a damage energy, through the Lindhard [46] model, which informed the Norgett-Robinson-Torrens (NRT-dpa) model [47, 48] used to determine the number of atomic displacements generated by any given cascade. This method is used to measure the applied dpa between steps.

High dose rates ($d\phi/dt \sim 1 \text{ dpa}/50 \text{ ns}$) are present in this simulation due to the time limitations of MD simulations, effectively meaning that the MD simulations will only show fast processes, such as Stage I and II recovery, but slow processes with high thermal barriers will be missed. Hence, the cascade simulations are propagated in the athermal regime. This has previously produced a credible representation of irradiated material [34] and is also suitable for comparison with room temperature experimental data on iron.

2.2. Computational Analysis

The OVITO code [49] was also used for the analysis. Polyhedral template matching (PTM) was used to determine local atomic orientations [50], which were fed into the grain segmentation modifier to identify which atoms were part of which grains. To calculate the mean excess potential energy per grain, the excess potential energy of each atom in the grain is calculated, and a mean over all the atoms is taken. The excess potential energy of the entire simulation cell is also calculated using LAMMPS. Excess is taken to mean the potential energy, in eV/atom, of a given grain or cell subtracted from the potential energy of a pristine, defect free iron cell, at room temperature with traction free boundary conditions.

3. Results

Figure 1 shows the mean grain number as a function of dose for all initially nanocrystalline iron cells, averaged over the five distinct simulations of each type of starting microstructure. A clear irradiation induced annealing process is shown whereby the grains in all the initially nanocrystalline cells

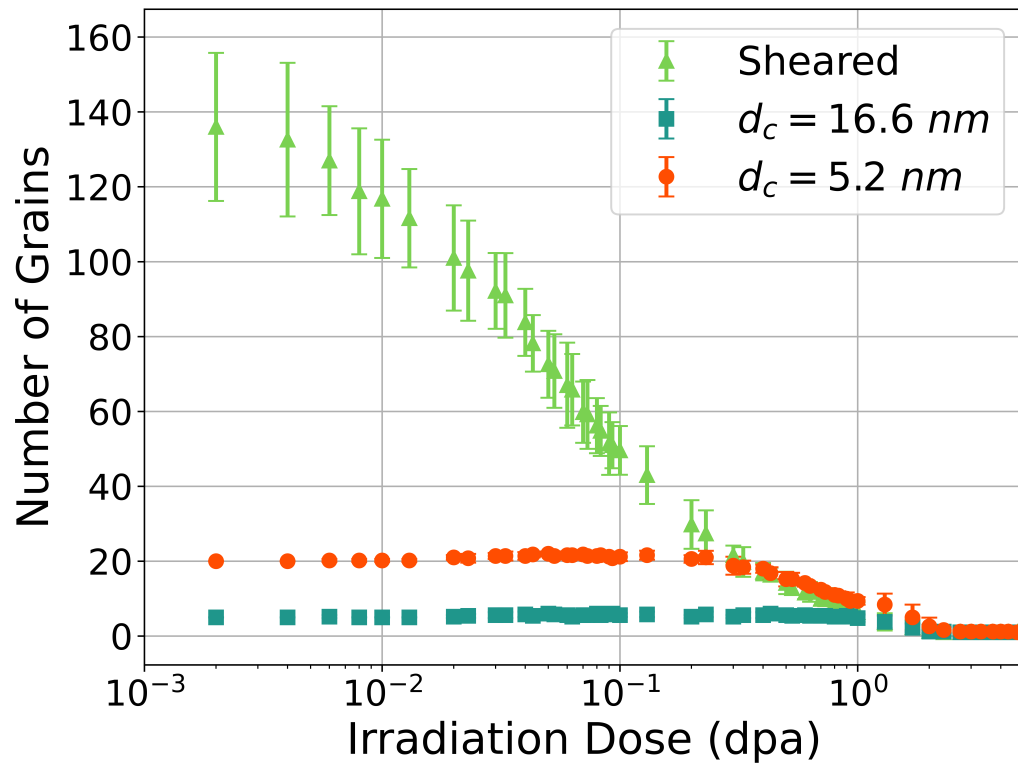


Figure 1: Grain number, obtained using grain segmentation in Ovito, as a function of dose for all initially nanocrystalline cells. A grain was taken to be a minimum of 100 atoms.

grow and become single crystalline after ~ 2 dpa. In Tolkachev *et al.* [28], which uses the same dataset, the irradiation induced grain growth was found to be consistent with random grain growth. Furthermore, the study [28] confirmed irradiation induced grain growth experimentally in self-ion irradiated, nanocrystalline iron.

Similar behaviour has previously been observed using molecular dynamics simulations [26, 27]. Ma *et al.* [26] observed irradiation induced grain growth in nanocrystalline tungsten, whilst Levo *et al.* [27] showed a grain growth in nanocrystalline nickel, with all cells becoming single crystalline with increased dose. Experimentally, irradiation induced annealing has also been observed in numerous studies [5, 13, 23, 24, 25].

Excess potential energy versus dose is plotted in Figure 2. The initially pristine cells are also added here for comparison. Figure 2(a) shows the overall excess potential energy, in eV/atom, for each starting configuration averaged over five independent simulations. As expected, at 0.001 dpa, the sheared cells have the highest excess energy due to the large number of grain boundaries and defects present within the cells. The $d_c = 5.2$ nm cells have the next highest, followed by the $d_c = 16.6$ nm cells, which is again expected as having smaller grains and more grain boundaries will raise the excess potential energy.

All initially nanocrystalline cells follow a similar trend; excess potential energy increases before decreasing and seemingly plateauing at similar values above ~ 4 dpa. This is more evident in Figure 2(b) which shows a zoomed in view of excess potential energy between 2 and 5 dpa. It is noticeable, particularly after 4.5 dpa, that the excess potential energy in the initially nanocrystalline cells seemingly converges at similar values of $\sim 0.022 - 0.023$ eV/atom, with much overlap in the standard deviations. This seems to suggest that, irrespective of the initial starting configuration, all initially nanocrystalline cells will converge at similar values of excess potential energy at high doses.

In Figure 2(a), the initially pristine cells do not follow the trend of the initially nanocrystalline cells, and the excess potential energy only increases with dose. Interestingly, the excess potential energy of the pristine cells nearly matches that of the initially nanocrystalline cells, being ~ 0.021 eV/atom at 5 dpa. We also note that the excess potential energy in the pristine cells is seemingly still increasing at 5 dpa and hypothesise that it will continue to increase until it reaches the range of the initially nanocrystalline cells.

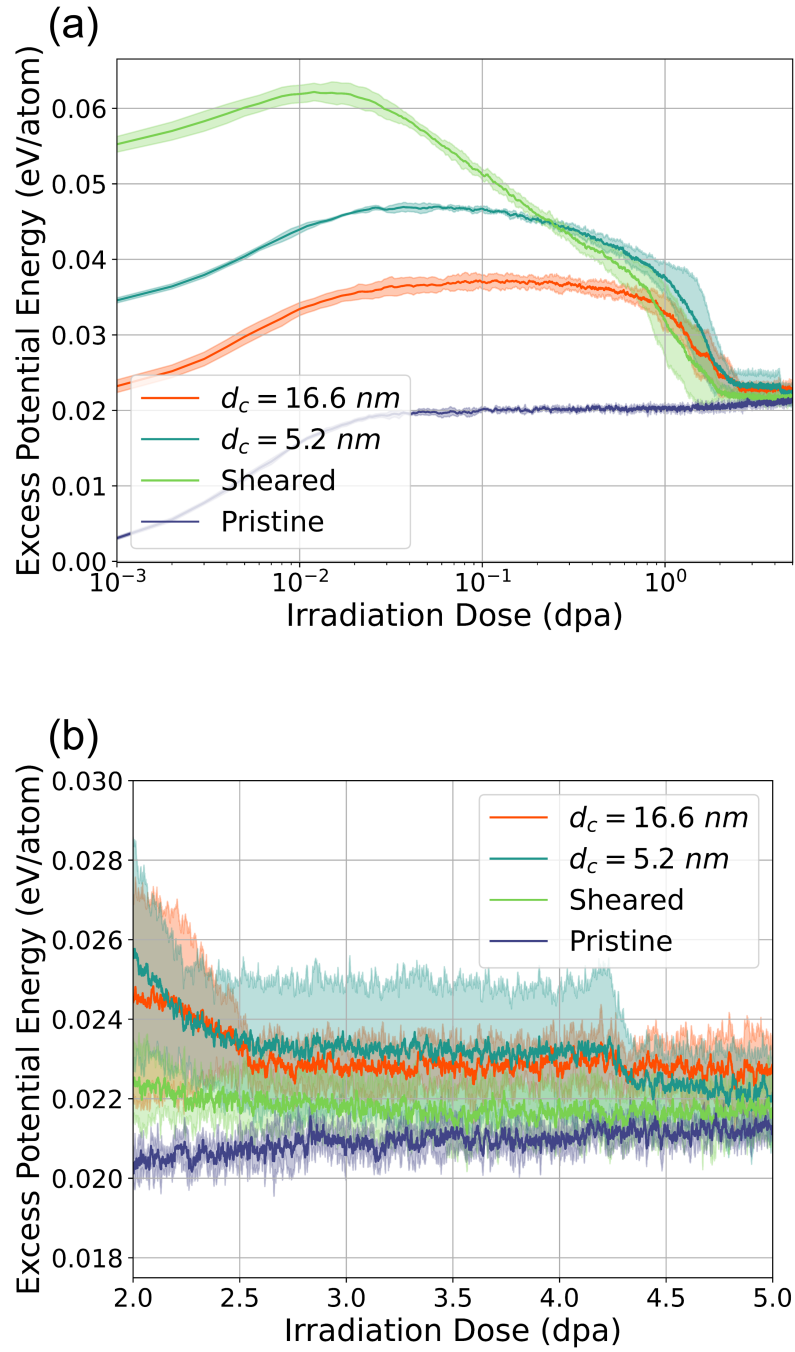


Figure 2: Excess potential energy versus dose for initially nanocrystalline and pristine cells in eV/atom; (a) Plotted between 10^{-3} dpa and 5 dpa, (b) Plotted between 2 dpa and 5 dpa.

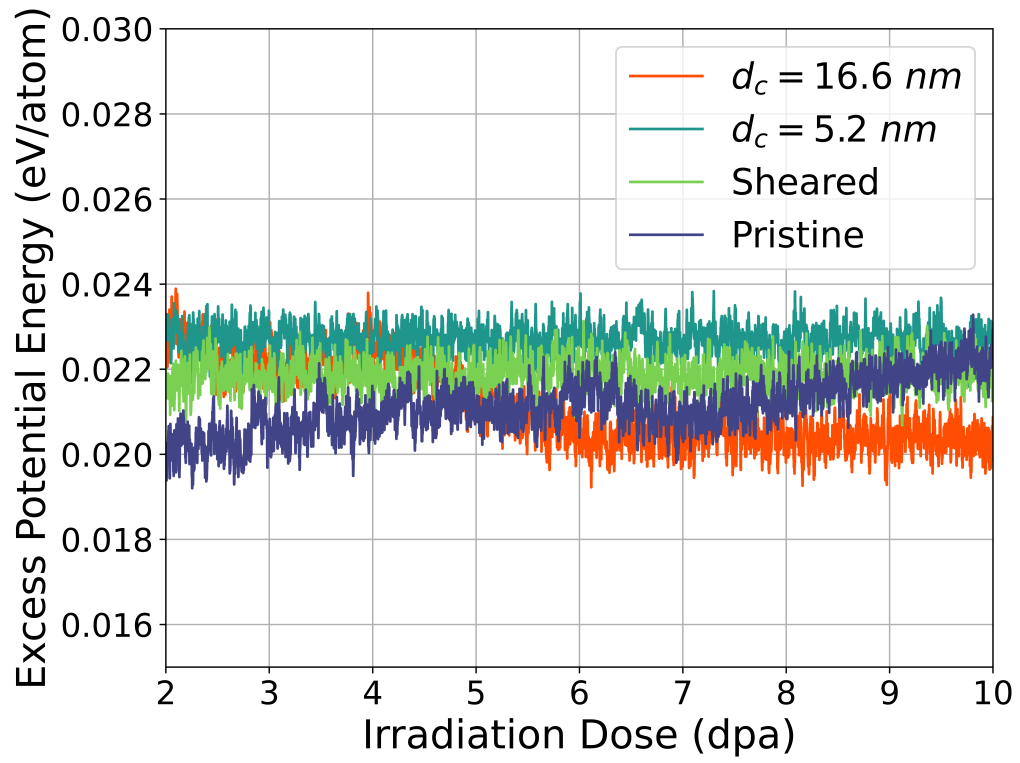


Figure 3: Damage against excess potential energy for a single instance of each simulation type between 2 and 10 dpa.

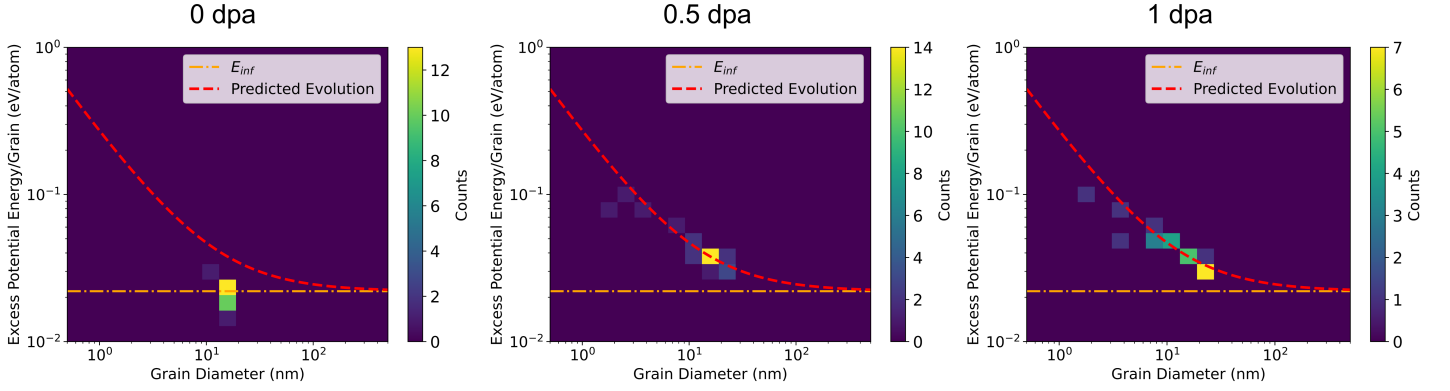
To test this hypothesis, a single instance of each simulation type was run to a damage of 10 dpa and the excess potential energy for these simulations, between 2 and 10 dpa, is shown in Figure 3. It is noticeable that both the sheared and $d_c = 5.2$ nm cells have plateaued beyond 2 dpa at ~ 0.022 eV/atom. However, the pristine cells is at 0.020 eV/atom at 2 dpa, and rises to 0.022 eV/atom by 9.5 dpa, seemingly plateauing after this dose. This seems to confirm the hypothesis above, whereby all simulation cell types will converge to a similar excess potential energy at high dose, irrespective of their initial starting configuration. Figure 3 does however show that the excess potential energy for the $d_c = 16.6$ nm cell reduces to ~ 0.020 eV/atom after 6 dpa and plateaus here. It is not immediately obvious why this occurs however, this variation is on the same scale as simulation-to-simulation fluctuations.

To evaluate how the excess potential energy evolves for individual grains, histograms of excess energy versus grain size for all simulations are presented in Figure 4. In Figure 4(a), the data for the $d_c = 16.6$ nm cells is shown. Initially, at 0 dpa, all grains have similar excess energy and size. By 0.5 dpa, there is a noticeable grain growth, with some grains getting larger. Note here, that some grains get smaller, corresponding to a higher excess energy. By 1 dpa, there are more larger grains of lower energy and some smaller grains of higher energy. Figure 4(b) shows the same data for the $d_c = 5.2$ nm cells. Again, a similar grain growth process is observed, and a direct correlation between grain size and excess potential energy is visible. At 1 dpa, there are numerous larger grains with lower energy and smaller grains with higher energy, as with the $d_c = 16.6$ nm cells.

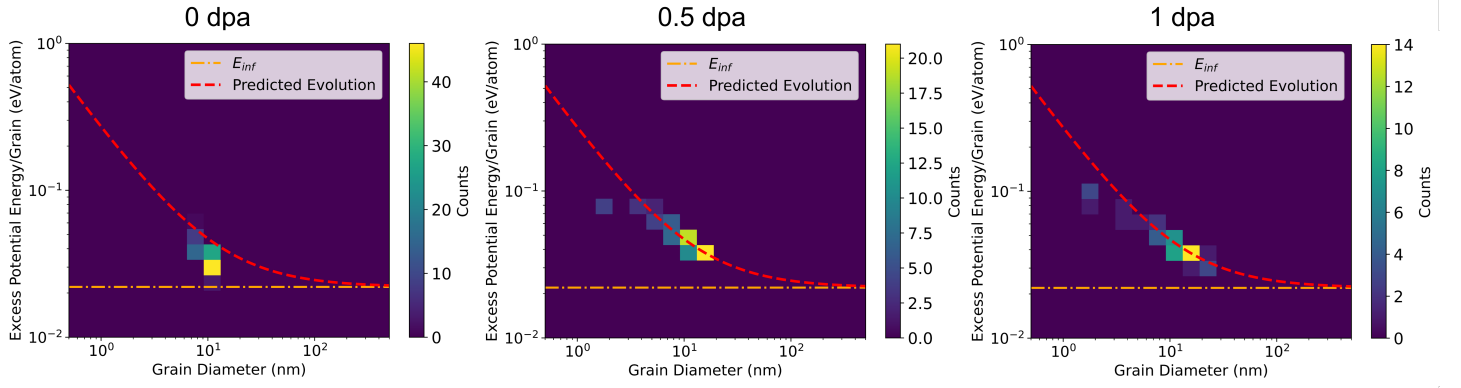
The data for the sheared cells in Figure 4(c) follows a different evolution. As in Figure 1, there are many more grains in the sheared cells, and this is reflected in the 0 dpa figure. By 0.5 dpa, the number of large grains has increased, with some smaller grains of higher energy, and a noticeable decrease in grain number as per Figure 1. Note the similarity in histograms between all cell types at 1 dpa. Whilst the number of grains is different, there is a noticeable trend in evolution notwithstanding the starting microstructure.

Appendix A depicts the histogram data for all cells at 5 dpa, and this shows that the excess potential energy per grain does plateau at E_{inf} . At this dose, all cells are single crystalline so the grain diameter becomes arbitrary.

(a) $d_c = 16.6$ nm



(b) $d_c = 5.2$ nm



(c) - Sheared

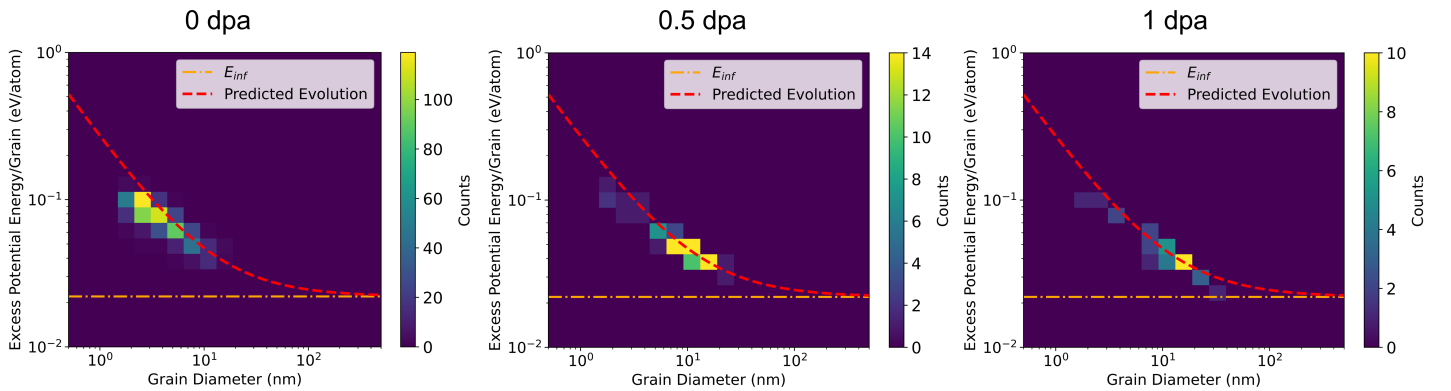


Figure 4: Excess potential energy histograms for individual grains for each starting nanocrystalline configuration; (a) $d_c = 16.6$ nm, (b) $d_c = 5.2$ nm, and (c) sheared cells.

4. Discussion

The molecular dynamics simulations presented in this work demonstrate a direct irradiation induced grain growth process as shown in Figure 1. This figure shows that the initially nanocrystalline cells experience a grain coarsening, and all become single crystalline after ~ 2 dpa. This is accompanied by a reduction in excess potential energy within grains as shown in Figure 4. In Figures 4(a) and 4(b), the Voronoi-generated cells start off with evenly sized grains of lower energy. At 0.5 dpa, some grains get larger, whilst some get smaller, but its noticeable that the excess potential energy in grains decreases with size increase.

Figure 4(c) shows the excess potential energy for the grains within the sheared cells at increasing doses. It is evident that the starting energies for these cells are very different to those of the Voronoi-generated cells. In fact, there are many small grains at 0 dpa with high energies, and this is also reflected in Figure 1 which shows the presence of many small grains in the sheared cells. Due to the nature of the cell creation, the grains within the sheared cells are expected to have higher energy as they have inherent material defects such as dislocations and interstitials as a result of the plastic deformation process. By 0.5 dpa, the irradiation induced annealing process leads to grain growth and the excess potential energy in most grains reduces as grain boundaries and other defects are annealed.

Interestingly, at 1 dpa, all histograms show that, irrespective of the initial configuration, all grains converge to a similar excess potential energy. This is also shown in Figure 2(a) which shows the excess potential energy for all cell types, averaged over five distinct simulations. Whilst the initially nanocrystalline cells behave differently at low doses, it is noticeable that their excess potential energy converges at higher doses.

Figure 2(b) shows that both Voronoi-generated and sheared cells converge to $\sim 0.022 - 0.023$ eV/atom by ~ 4.5 dpa, with overlapping standard deviations across all five simulation types. Pristine cells, by contrast, exhibit a continuous rise in excess potential energy with dose. Extending one simulation of each cell type to 10 dpa (Figure 3) confirms that the pristine cell's energy keeps increasing until ~ 9.5 dpa, then plateaus at ~ 0.022 eV/atom.

To explain this behaviour, we develop a hypothesis on how the excess potential energy in the grains is dependent on grain size, when driven by collision cascades. It is proposed, based on the observable data in Figure 4, that when grains are smaller, the size of the grain dominates the excess

potential energy within that grain giving:

$$E = Ad^{-\phi} \quad (1)$$

where E is excess potential energy density, $-\phi$ is a constant governing decay, d is grain size, and A is a constant of proportionality. It is noted from Figure 4 that at small grain size, the energy evolution looks linear. If we assume that the excess potential energy is dominated by grain boundary energy, then the energy per unit volume roughly scales with grain boundary energy/volume giving $\sim 1/d$. Hence, the value of $\phi = -1$.

We also propose that at some high dose, the size of the grains becomes irrelevant and that the radiation damage dominates the excess potential energy value instead. This is shown as E_{inf} in Figure 4. E_{inf} corresponds to the excess potential energy caused by radiation damage in the high dose limit, and is calculated by determining the excess potential energy in the pristine cell at 10 dpa in Figure 3, which was found to be 2.2×10^{-2} eV/atom.

This term is added as it is noticeable in Figure 4, and in the 5 dpa figures in Appendix A, that the excess potential energy per grain does plateau at E_{inf} . At this dose, all cells are single crystalline so the grain diameter becomes arbitrary. Hence, the predicted evolution becomes:

$$E = Ad^{-1} + E_{inf} \quad (2)$$

The value of A was determined to be $0.307 \pm 8.972 \times 10^{-4}$ eVnm when fitting and keeping $\phi = -1$. The fitting method is shown in Figure 5. The pure Ad^{-1} part is found by fitting data to the energy of grains of various sizes generated through Voronoi tessellation and relaxed. These represent perfect, defect free grains without the involvement of radiation damage. The extra E_{inf} term captures the added effect of irradiation damage in the limit of an infinite crystal, as discussed above. Nonetheless, when plotting Figure 4, and carrying out the fitting in Figure 5, the values of ϕ was set to -1 . The value of A was analytically determined in Appendix B, and was found to be in the range of $A = 0.219 - 0.489$ eVnm, which coincides well with the fitted value of $A = 0.307$ eVnm, giving confidence to the fitting.

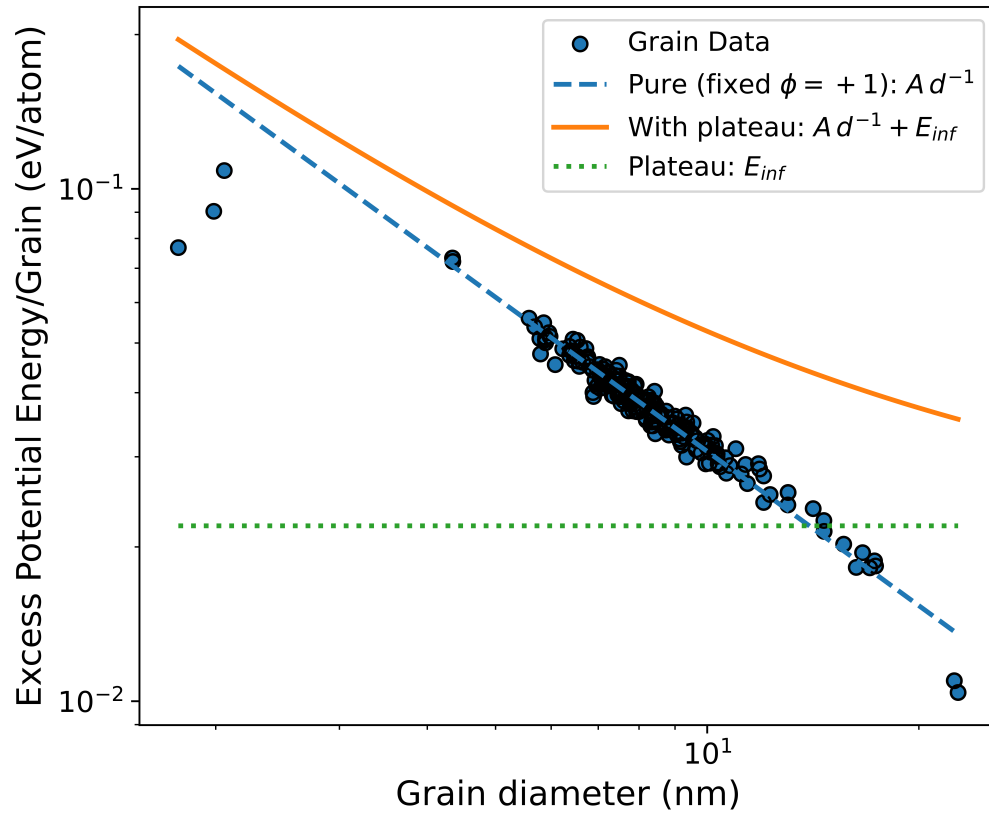


Figure 5: Predicted evolution of excess potential energy with increasing grain size fitting.

It is noticeable, from Figure 4, that the model is able to predict the observed excess potential energy evolution in the grains of the nanocrystalline material. Appendix A shows that, at 5 dpa, all grains plateau at the value of E_{inf} . Note, that the grain here becomes infinitely large as the MD simulation cells become single crystalline after ~ 2 dpa, as shown in Figure 1.

Our results suggest that, from an energetic perspective, all initially nanocrystalline cells will converge to similar excess potential energy at high doses, notwithstanding their differing initial configurations and subsequent evolution at low doses. Furthermore, it appears that an initially pristine cell will also reach the same energetic state as the initially nanocrystalline cells in the high dose limit.

5. Conclusion

We have studied the energy evolution of both initially nanocrystalline and pristine cells subjected to cascade damage using MD simulations. The nanocrystalline cells were created through both Voronoi tessellation and plastic shearing deformation. Subsequently, our results allow the following conclusions:

- An irradiation induced annealing process was observed whereby all initially nanocrystalline cells became single crystalline after ~ 2 dpa.
- The annealing was further confirmed by considering the excess potential energy in individual grains for the initially nanocrystalline iron cells. All cell types showed that larger grains tended to have lower excess potential energy than smaller grains.
- A model was derived to explain the evolution of excess potential energy within the grains with irradiation as some grains increased in size and some became smaller. This was found to correlate well with the observed energy data for the grains in the MD simulation cells.
- This trend is further shown when looking at the excess potential energy in the cells. Whilst at low doses, all initially nanocrystalline cells have differing evolution, at doses above ~ 4 dpa, the excess potential energy in all cells seemingly converges. Interestingly, the pristine cells also reach a similar value of excess potential energy at 5 dpa, albeit slightly lower. It was noticeable that the excess potential energy in the initially

pristine cells was still increasing at 5 dpa. We hypothesised that the energy would continue increasing at higher doses to the same level of the initially nanocrystalline cells. A single instance of each cell type was run to a dose of 10 dpa to test this hypothesis. This data showed that the pristine cell’s excess potential energy plateaued at the same point as some of the initially nanocrystalline cells after ~ 9.5 dpa.

- All data seems to point to the fact that, irrespective of initial cell configuration, from an energetic perspective, all cells will converge at near identical values at high doses.

6. Data Availability

All input scripts and simulation data presented in the current work are available at *A link will be provided after the review process and before publication.*

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Appendix A. Histogram Data at 5 dpa

Figure A.6 depicts the histograms of excess potential energy in the grains at 5 dpa for each initial simulation cell condition. At this dose, all grains are

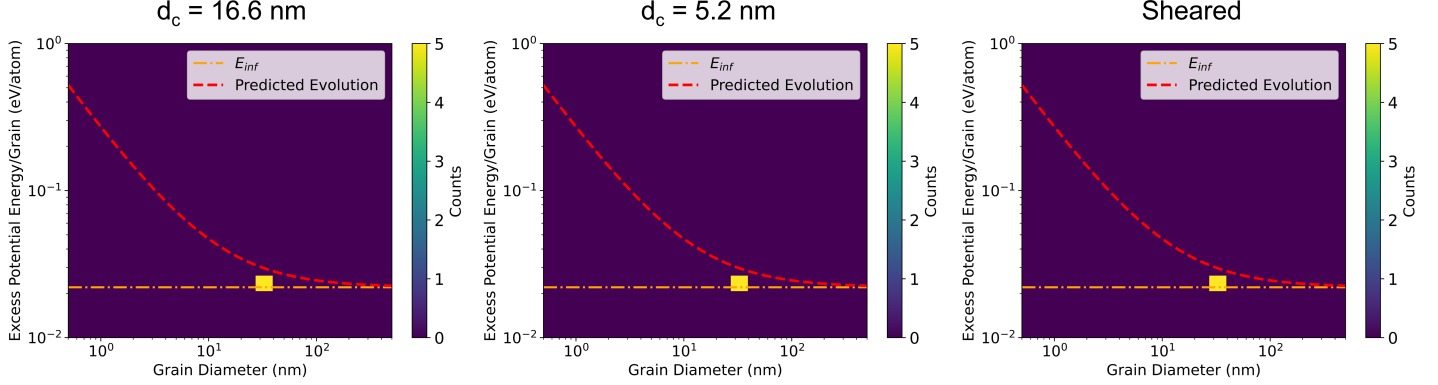


Figure A.6: Histograms of excess potential energy versus grain diameter at 5 dpa for all initial starting configurations. By this dose, all cells are single crystalline which means that grain diameter is the same as the cell size, corresponding to the single crystal limit.

single crystalline and due to periodic boundary conditions, grains diameter becomes arbitrary. Nonetheless, the box size is 28 nm x 28 nm x 28 nm, and hence, this shows as the grain diameter. The histograms show that at high dose, the initially nanocrystalline cells all converge on the value of E_{inf} .

Appendix B. Analytical Analysis for Proportionality Constant

As mentioned before, the fitted value of A was found to be $0.307 \pm 8.972 \times 10^{-4}$ eVnm. To determine whether this value is suitable, an analytical analysis was carried out as below.

Firstly, we start with the equation $E = Ad^{-1}$ which is the grain boundary dominant term of the full model in Equation 2. Assuming grains are spherical, and since the grain boundaries dominate, this equation can be rewritten as:

$$E = \frac{4\pi\left(\frac{d^2}{2}\right) \times e_{GB} \times \frac{1}{2}}{\frac{4}{3}\pi\left(\frac{d}{2}\right)^3} \quad (\text{B.1})$$

Here, the numerator contains the area of a spherical grain, the energy of grain boundaries per unit area, e_{GB} , and the $\frac{1}{2}$ factor as the grain boundary

is shared between two grains. The denominator simply contains the volume of the grain. This simply reduces down to:

$$E = \frac{3e_{GB}}{d} \quad (\text{B.2})$$

giving, $A = 3e_{GB}$. If we convert this to a per atom value we get:

$$A = 3e_{GB} \times \text{atomic volume} = \frac{3}{2}e_{GB} a_0^3 \quad (\text{B.3})$$

A reasonable figure for the energy of grain boundaries, e_{GB} , in alpha iron is around $1 - 1.5 \text{ J/m}^2$ [51, 52, 53], and when taking $a_0 = 0.286 \text{ nm}$ for alpha iron, the range of A becomes $0.219 - 0.329 \text{ eVnm}$. Now we assume that the grain are not spherical and instead are cubes. To find an equivalent volume per grain, the following equation is utilised:

$$V_{sphere} = \frac{4}{3}\pi\left(\frac{d}{2}\right)^3 = \frac{1}{6}\pi d^3 = w^3 \quad (\text{B.4})$$

where w is the side length of a cube. It follows then that:

$$w = \sqrt[3]{\frac{\pi}{6}} d \quad (\text{B.5})$$

Hence, following the same procedure as above, the value of E becomes:

$$E = 3\sqrt[3]{\frac{6}{\pi}} \frac{1}{d}e_{GB} = 3.72 e_{GB} \frac{1}{d} \quad (\text{B.6})$$

Therefore, in the case of the cube grain assumption, the value of A becomes $0.272 - 0.408 \text{ eVnm}$. Finally, the grains are assumed to be tetrahedrons and an equivalent volume is found compared to the spherical grain approximation. It then follows:

$$V_{sphere} = \frac{1}{6}\pi d^3 = \frac{a^3}{6\sqrt{2}} \quad (\text{B.7})$$

where a is the length of the edge. It then follows that:

$$a = (\sqrt{2}\pi)^{\frac{1}{3}}d \quad (\text{B.8})$$

As such, we again follow the same procedure as above, and the value of E becomes:

$$E = \frac{\sqrt{6} \ 3}{(\sqrt{2}\pi)^{\frac{1}{3}}} \frac{1}{d} e_{GB} = 4.47 \ e_{GB} \frac{1}{d} \quad (\text{B.9})$$

Hence, when taking an equivalent volume to the spherical approximation, when assuming the grains are tetrahedrons, the value of A becomes 0.326 – 0.489 eVnm.

All in all, notwithstanding the approximation of grain shape, the fitted value of $A = 0.307 \pm 8.972 \times 10^{-4}$ eVnm is coincident with the expected values obtained through an analytical analysis, which gives confidence to the fitting the grain evolution model.

References

- [1] R. J. Kurtz, G. R. Odette, Chapter 3 - overview of reactor systems and operational environments for structural materials in fusion reactors, in: G. R. Odette, S. J. Zinkle (Eds.), Structural Alloys for Nuclear Energy Applications, Elsevier, Boston, 2019, pp. 51–102. doi:<https://doi.org/10.1016/B978-0-12-397046-6.00003-4>. URL <https://www.sciencedirect.com/science/article/pii/B9780123970466000034>
- [2] M. Gilbert, J. Marian, J.-C. Sublet, Energy spectra of primary knock-on atoms under neutron irradiation, Journal of Nuclear Materials 467 (2015) 121–134. doi:<https://doi.org/10.1016/j.jnucmat.2015.09.023>. URL <https://www.sciencedirect.com/science/article/pii/S0022311515302129>

- [3] A. Dubinko, D. Terentyev, C. Yin, W. Van Renterghem, B. Rossaert, M. Rieth, E. Zhurkin, A. Zinovev, C. Chang, S. Van Dyck, G. Bonny, Microstructure and hardening induced by neutron irradiation in single crystal, iter specification and cold rolled tungsten, *International Journal of Refractory Metals and Hard Materials* 98 (2021) 105522. doi:<https://doi.org/10.1016/j.ijrmhm.2021.105522>. URL <https://www.sciencedirect.com/science/article/pii/S0263436821000548>
- [4] K. Song, D. Sheyfer, K. Mizohata, M. Zhang, W. Liu, D. Gürsoy, D. Yang, I. Tolkachev, H. Yu, D. E. Armstrong, F. Hofmann, Dose and compositional dependence of irradiation-induced property change in fecr, *Journal of Nuclear Materials* 594 (2024) 154998. doi:<https://doi.org/10.1016/j.jnucmat.2024.154998>. URL <https://www.sciencedirect.com/science/article/pii/S0022311524001016>
- [5] K. Song, G. He, A. Reza, T. Ungár, P. Karamched, D. Yang, I. Tolkachev, K. Mizohata, S. P. Thompson, E. T. Connolly, R. C. Atwood, S. Michalik, D. E. Armstrong, F. Hofmann, Microstructural and material property changes in severely deformed eurofer-97, *Materials Characterization* 215 (2024) 114144. doi:<https://doi.org/10.1016/j.matchar.2024.114144>. URL <https://www.sciencedirect.com/science/article/pii/S1044580324005254>
- [6] A. Reza, G. He, C. A. Dennett, H. Yu, K. Mizohata, F. Hofmann, Thermal diffusivity recovery and defect annealing kinetics of self-ion implanted tungsten probed by insitu transient grating spectroscopy, *Acta Materialia* 232 (2022) 117926. doi:<https://doi.org/10.1016/j.actamat.2022.117926>. URL <https://www.sciencedirect.com/science/article/pii/S1359645422003081>
- [7] F. Hofmann, D. R. Mason, J. K. Eliason, A. A. Maznev, K. A. Nelson, S. L. Dudarev, Non-contact measurement of thermal diffusivity in ion-implanted nuclear materials, *Scientific Reports* 5 (05 2015). doi:[10.1038/srep16042](https://doi.org/10.1038/srep16042).
- [8] I. Beyerlein, M. Demkowicz, A. Misra, B. Uberuaga, Defect-interface interactions, *Progress in Materials Science* 74 (2015) 125–210. doi:<https://doi.org/10.1016/j.pmatsci.2015.02.001>. URL <https://www.sciencedirect.com/science/article/pii/S0079642515000225>

- [9] O. El-Atwani, J. Nathaniel, A. Leff, K. Hattar, M. Taheri, Direct observation of sink-dependent defect evolution in nanocrystalline iron under irradiation, *Scientific Reports* 7 (12 2017). doi:10.1038/s41598-017-01744-.
- [10] X.-M. Bai, A. F. Voter, R. G. Hoagland, M. Nastasi, B. P. Uberuaga, Efficient annealing of radiation damage near grain boundaries via interstitial emission, *Science* 327 (5973) (2010) 1631–1634. arXiv:<https://www.science.org/doi/pdf/10.1126/science.1183723>, doi:10.1126/science.1183723. URL <https://www.science.org/doi/abs/10.1126/science.1183723>
- [11] M. A. Tschopp, K. N. Solanki, F. Gao, X. Sun, M. A. Khaleel, M. F. Horstemeyer, Probing grain boundary sink strength at the nanoscale: Energetics and length scales of vacancy and interstitial absorption by grain boundaries in α -Fe, *Phys. Rev. B* 85 (2012) 064108. doi:10.1103/PhysRevB.85.064108. URL <https://link.aps.org/doi/10.1103/PhysRevB.85.064108>
- [12] M. Samaras, P. M. Derlet, H. Van Swygenhoven, M. Victoria, Computer simulation of displacement cascades in nanocrystalline Ni, *Phys. Rev. Lett.* 88 (2002) 125505. doi:10.1103/PhysRevLett.88.125505. URL <https://link.aps.org/doi/10.1103/PhysRevLett.88.125505>
- [13] N. Nita, R. Schaeublin, M. Victoria, Impact of irradiation on the microstructure of nanocrystalline materials, *Journal of Nuclear Materials* 329-333 (2004) 953–957, proceedings of the 11th International Conference on Fusion Reactor Materials (ICFRM-11). doi:<https://doi.org/10.1016/j.jnucmat.2004.04.058>. URL <https://www.sciencedirect.com/science/article/pii/S0022311504002004>
- [14] Y. Chimi, A. Iwase, N. Ishikawa, M. Kobiyama, T. Inami, S. Okuda, Accumulation and recovery of defects in ion-irradiated nanocrystalline gold, *Journal of Nuclear Materials* 297 (3) (2001) 355–357. doi:[https://doi.org/10.1016/S0022-3115\(01\)00629-8](https://doi.org/10.1016/S0022-3115(01)00629-8). URL <https://www.sciencedirect.com/science/article/pii/S0022311501006298>
- [15] K. M. Agarwal, R. K. Tyagi, V. K. Chaubey, A. Dixit, Comparison of different methods of severe plastic deformation for grain refinement, *IOP Conference Series: Materials Science and Engineering* 691 (2019)

012074. doi:10.1088/1757-899X/691/1/012074.
URL <https://iopscience.iop.org/article/10.1088/1757-899X/691/1/012074>
- [16] M. Borodachenkova, W. Wen, A. M. de Bastos Pereira, High-Pressure Torsion: Experiments and Modeling, IntechOpen, Rijeka, 2017, Ch. 4. doi:10.5772/intechopen.69173.
URL <https://doi.org/10.5772/intechopen.69173>
- [17] A. Zhilyaev, K. Oh-ishi, T. Langdon, T. McNelley, Microstructural evolution in commercial purity aluminum during high-pressure torsion, Materials Science and Engineering: A 410-411 (2005) 277–280, the Langdon Symposium: Flow and forming of Crystalline Materials. doi:<https://doi.org/10.1016/j.msea.2005.08.044>.
URL <https://www.sciencedirect.com/science/article/pii/S0921509305008397>
- [18] Y. Ito, Z. Horita, Microstructural evolution in pure aluminum processed by high-pressure torsion, Materials Science and Engineering: A 503 (1) (2009) 32–36, international Symposium on Bulk Nanostructured Materials: from Fundamentals to Innovation, BNM 2007. doi:<https://doi.org/10.1016/j.msea.2008.03.055>.
URL <https://www.sciencedirect.com/science/article/pii/S0921509308008939>
- [19] G. Strangward-Pryce, K. Song, K. Mizohata, F. Hofmann, The effect of high-pressure torsion on irradiation hardening of eurofer-97, Nuclear Materials and Energy 36 (2023) 101468. doi:<https://doi.org/10.1016/j.nme.2023.101468>.
URL <https://www.sciencedirect.com/science/article/pii/S2352179123001072>
- [20] G. Voronoi, Nouvelles applications des paramètres continus à la théorie des formes quadratiques. premier mémoire. sur quelques propriétés des formes quadratiques positives parfaites., Journal für die reine und angewandte Mathematik 133 (1908) 97–178.
URL <http://eudml.org/doc/149276>
- [21] I. Tolkachev, P.-W. Ma, D. R. Mason, F. Hofmann, Simulations of nanocrystalline iron formation under high shear strain, Phys. Rev. Mater. 9 (2025) 016001. doi:10.1103/PhysRevMaterials.9.016001.
URL <https://link.aps.org/doi/10.1103/PhysRevMaterials.9.016001>

- [22] X.-X. Guo, D.-D. Jiang, J.-L. Shao, Atomistic simulation of structural transition and grain refinement in Fe nanowires driven by high strain rate compression, *Journal of Applied Physics* 135 (3) (2024) 035102. doi:10.1063/5.0176619.
URL <https://doi.org/10.1063/5.0176619>
- [23] H. A. Atwater, C. V. Thompson, H. I. Smith, Ion-bombardment-enhanced grain growth in germanium, silicon, and gold thin films, *Journal of Applied Physics* 64 (5) (1988) 2337–2353. arXiv:https://pubs.aip.org/aip/jap/article-pdf/64/5/2337/18619198/2337_1_online.pdf, doi:10.1063/1.341665.
URL <https://doi.org/10.1063/1.341665>
- [24] D. Kaoumi, A. T. Motta, R. C. Birtcher, A thermal spike model of grain growth under irradiation, *Journal of Applied Physics* 104 (7) (2008) 073525. arXiv:https://pubs.aip.org/aip/jap/article-pdf/doi/10.1063/1.2988142/15021068/073525_1_online.pdf, doi:10.1063/1.2988142.
URL <https://doi.org/10.1063/1.2988142>
- [25] D. C. Bufford, F. F. Abdeljawad, S. M. Foiles, K. Hattar, Unraveling irradiation induced grain growth with in situ transmission electron microscopy and coordinated modeling, *Applied Physics Letters* 107 (19) (2015) 191901. arXiv:https://pubs.aip.org/aip/apl/article-pdf/doi/10.1063/1.4935238/13654381/191901_1_online.pdf, doi:10.1063/1.4935238.
URL <https://doi.org/10.1063/1.4935238>
- [26] P.-W. Ma, D. R. Mason, S. Van Boxel, S. L. Dudarev, Nanocrystalline tungsten at high radiation exposure, *Phys. Rev. Mater.* 8 (2024) 083601. doi:10.1103/PhysRevMaterials.8.083601.
URL <https://link.aps.org/doi/10.1103/PhysRevMaterials.8.083601>
- [27] E. Levo, F. Granberg, D. Utt, K. Nordlund, F. Djurabekova, Radiation stability of nanocrystalline single-phase multicomponent alloys, *Journal of Materials Research* 34 (2019) 854–866. doi:10.1557/jmr.2019.19.
- [28] I. Tolkachev, D. R. Mason, M. Boleininger, P.-W. Ma, D. Long, E. T. Connolly, S. P. Thompson, K. Mizohata, F. Hofmann, Atomistic and experimental study of microstructural evolution in nanocrystalline iron

- subjected to irradiation (2025). arXiv:2505.21174.
URL <https://arxiv.org/abs/2505.21174>
- [29] P. M. Derlet, S. L. Dudarev, Microscopic structure of a heavily irradiated material, *Phys. Rev. Mater.* 4 (2020) 023605. doi:10.1103/PhysRevMaterials.4.023605.
URL <https://link.aps.org/doi/10.1103/PhysRevMaterials.4.023605>
 - [30] F. A. Garner, M. B. Toloczko, B. H. Sencer, Comparison of swelling and irradiation creep behavior of fcc-austenitic and bcc-ferritic/martensitic alloys at high neutron exposure, *Journal of Nuclear Materials* 276 (1) (2000) 123–142. doi:[https://doi.org/10.1016/S0022-3115\(99\)00225-1](https://doi.org/10.1016/S0022-3115(99)00225-1).
URL <https://www.sciencedirect.com/science/article/pii/S0022311599002251>
 - [31] J.-L. Boutard, A. Alamo, R. Lindau, M. Rieth, Fissile core and Tritium-Breeding Blanket: structural materials and their requirements, *Comptes Rendus. Physique* 9 (3-4) (2008) 287–302. doi:10.1016/j.crhy.2007.11.004.
 - [32] C. Cabet, F. Dalle, E. Gaganidze, J. Henry, H. Tanigawa, Ferritic-martensitic steels for fission and fusion applications, *Journal of Nuclear Materials* 523 (2019) 510–537. doi:<https://doi.org/10.1016/j.jnucmat.2019.05.058>.
URL <https://www.sciencedirect.com/science/article/pii/S0022311519301990>
 - [33] G. Mazzone, J. Aktaa, C. Bachmann, D. De Meis, P. Frosi, E. Gaganidze, G. Di Gironimo, G. Mariano, D. Marzullo, M. Porfiri, M. Rieth, R. Villari, J. You, Choice of a low operating temperature for the demo eurofer97 divertor cassette, *Fusion Engineering and Design* 124 (2017) 655–658, proceedings of the 29th Symposium on Fusion Technology (SOFT-29) Prague, Czech Republic, September 5-9, 2016. doi:<https://doi.org/10.1016/j.fusengdes.2017.02.013>.
URL <https://www.sciencedirect.com/science/article/pii/S0920379617300960>
 - [34] M. Boleininger, D. R. Mason, A. E. Sand, S. L. Dudarev, Microstructure of a heavily irradiated metal exposed to a spectrum of atomic recoils, *Scientific Reports* 13 (01 2023). doi:10.1038/s41598-022-27087-w.
 - [35] F. Granberg, J. Byggmästar, K. Nordlund, Defect accumulation and evolution during prolonged irradiation of fe and

- fecr alloys, *Journal of Nuclear Materials* 528 (2020) 151843.
doi:<https://doi.org/10.1016/j.jnucmat.2019.151843>.
URL <https://www.sciencedirect.com/science/article/pii/S0022311519305719>
- [36] A. Sand, J. Byggmästar, A. Zitting, K. Nordlund, Defect structures and statistics in overlapping cascade damage in fusion-relevant bcc metals, *Journal of Nuclear Materials* 511 (2018) 64–74, special Section on "18th International Conference on Fusion Reactor Materials".
doi:<https://doi.org/10.1016/j.jnucmat.2018.08.049>.
URL <https://www.sciencedirect.com/science/article/pii/S0022311518305178>
- [37] F. Granberg, K. Nordlund, M. W. Ullah, K. Jin, C. Lu, H. Bei, L. M. Wang, F. Djurabekova, W. J. Weber, Y. Zhang, Mechanism of radiation damage reduction in equiatomic multicomponent single phase alloys, *Phys. Rev. Lett.* 116 (2016) 135504.
doi:[10.1103/PhysRevLett.116.135504](https://doi.org/10.1103/PhysRevLett.116.135504).
URL <https://link.aps.org/doi/10.1103/PhysRevLett.116.135504>
- [38] A. P. Thompson, H. M. Aktulga, R. Berger, D. S. Bolintineanu, W. M. Brown, P. S. Crozier, P. J. in 't Veld, A. Kohlmeyer, S. G. Moore, T. D. Nguyen, R. Shan, M. J. Stevens, J. Tranchida, C. Trott, S. J. Plimpton, LAMMPS - a flexible simulation tool for particle-based materials modeling at the atomic, meso, and continuum scales, *Computer Physics Communications* 271 (2022) 108171.
doi:<https://doi.org/10.1016/j.cpc.2021.108171>.
URL <https://www.sciencedirect.com/science/article/pii/S0010465521002836>
- [39] J.-S. Ferenc, Z. Nédá, On the size distribution of poisson voronoi cells, *Physica A: Statistical Mechanics and its Applications* 385 (2) (2007) 518–526. doi:<https://doi.org/10.1016/j.physa.2007.07.063>.
URL <https://www.sciencedirect.com/science/article/pii/S0378437107007546>
- [40] B. Mandelbrot, An informational theory of the statistical structure of language, *Communication Theory* (1953) 486–502.
- [41] M. I. Mendelev, S. Han, D. J. Srolovitz, G. J. Ackland, D. Y. Sun, M. Asta, Development of new interatomic potentials appropriate for crystalline and liquid iron, *Philosophical Magazine* 83 (35) (2003) 3977–3994. arXiv:<https://doi.org/10.1080/14786430310001613264>,

doi:10.1080/14786430310001613264.

URL <https://doi.org/10.1080/14786430310001613264>

- [42] A. Kedharnath, R. Kapoor, A. Sarkar, Atomistic simulation of interaction of collision cascade with different types of grain boundaries in alpha-fe, *Journal of Nuclear Materials* 523 (2019) 444–457. doi:<https://doi.org/10.1016/j.jnucmat.2019.06.021>. URL <https://www.sciencedirect.com/science/article/pii/S0022311518313266>
- [43] T. Ye, H. Yao, Y. Wu, J. Zhang, J. Wu, M. Wang, W. Tian, G. Su, S. Qiu, Primary radiation damage characteristics in displacement cascades of ferral alloys, *Journal of Nuclear Materials* 549 (2021) 152909. doi:<https://doi.org/10.1016/j.jnucmat.2021.152909>. URL <https://www.sciencedirect.com/science/article/pii/S0022311521001331>
- [44] L. Malerba, M. Marinica, N. Anento, C. Björkas, H. Nguyen, C. Domain, F. Djurabekova, P. Olsson, K. Nordlund, A. Serra, D. Terentyev, F. Willaime, C. Becquart, Comparison of empirical interatomic potentials for iron applied to radiation damage studies, *Journal of Nuclear Materials* 406 (1) (2010) 19–38, fP6 IP PERFECT Project: Prediction of Irradiation Damage Effects in Reactor Components. doi:<https://doi.org/10.1016/j.jnucmat.2010.05.017>. URL <https://www.sciencedirect.com/science/article/pii/S0022311510002291>
- [45] J. F. Ziegler, Srim-2003, Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms 219-220 (2004) 1027–1036, proceedings of the Sixteenth International Conference on Ion Beam Analysis. doi:<https://doi.org/10.1016/j.nimb.2004.01.208>. URL <https://www.sciencedirect.com/science/article/pii/S0168583X04002587>
- [46] J. Lindhard, M. Scharff, Energy dissipation by ions in the kev region, *Phys. Rev.* 124 (1961) 128–130. doi:10.1103/PhysRev.124.128. URL <https://link.aps.org/doi/10.1103/PhysRev.124.128>
- [47] M. T. Robinson, I. M. Torrens, Computer simulation of atomic-displacement cascades in solids in the binary-collision approximation, *Phys. Rev. B* 9 (1974) 5008–5024. doi:10.1103/PhysRevB.9.5008. URL <https://link.aps.org/doi/10.1103/PhysRevB.9.5008>

- [48] M. Norgett, M. Robinson, I. Torrens, A proposed method of calculating displacement dose rates, *Nuclear Engineering and Design* 33 (1) (1975) 50–54. doi:[https://doi.org/10.1016/0029-5493\(75\)90035-7](https://doi.org/10.1016/0029-5493(75)90035-7).
URL <https://www.sciencedirect.com/science/article/pii/0029549375900357>
- [49] A. Stukowski, Visualization and analysis of atomistic simulation data with ovito—the open visualization tool, *Modelling and Simulation in Materials Science and Engineering* 18 (1) (2009) 015012. doi:10.1088/0965-0393/18/1/015012.
URL <https://dx.doi.org/10.1088/0965-0393/18/1/015012>
- [50] P. M. Larsen, S. Schmidt, J. Schiøtz, Robust structural identification via polyhedral template matching, *Modelling and Simulation in Materials Science and Engineering* 24 (5) (2016) 055007. doi:10.1088/0965-0393/24/5/055007.
URL <https://dx.doi.org/10.1088/0965-0393/24/5/055007>
- [51] R. Sarochawikasit, C. Wang, P. Kumam, H. Beladi, T. Okita, G. S. Rohrer, S. Ratanaphan, Grain boundary energy function for α iron, *Materialia* 19 (2021) 101186. doi:<https://doi.org/10.1016/j.mtla.2021.101186>.
URL <https://www.sciencedirect.com/science/article/pii/S2589152921001897>
- [52] Y. Shiihara, R. Kanazawa, D. Matsunaka, I. Lobzenko, T. Tsuru, M. Kohyama, H. Mori, Artificial neural network molecular mechanics of iron grain boundaries, *Scripta Materialia* 207 (2022) 114268. doi:<https://doi.org/10.1016/j.scriptamat.2021.114268>.
URL <https://www.sciencedirect.com/science/article/pii/S1359646221005480>
- [53] M. Rajagopalan, M. Tschopp, K. Solanki, Grain boundary segregation of interstitial and substitutional impurity atoms in alpha-iron, *The Journal of The Minerals, Metals & Materials Society* 66 (2014) 129–138. doi:<https://doi.org/10.1007/s11837-013-0807-9>.
URL <https://link.springer.com/article/10.1007/s11837-013-0807-9>