Identification of dominant damage accumulation processes at grain boundaries during irradiation in nanocrystalline α -Fe: a statistical study

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Abstract

Radiation defect accumulation in metals with high interface to volume ratios, such as nanocrystalline metals, is strongly dependent on the ability of these interfaces to act as unbiased sinks for defects. Multi-scale simulations of damage accumulation in such materials necessarily depend on parameters describing defect behaviors inside grain boundaries, such as migration and binding energies within grain boundaries as well as binding energies of defects to grain boundaries. In general, these behaviors are sensitive to the grain boundary structure, making atomic-scale quantification of such parameters challenging due to the large number of variables in the input space of such a problem. The goal of the present study is to identify which of these parameters most strongly influence defect accumulation and grain boundary sink efficiency in α -Fe during Frenkel pair implantation at room temperature and a dose rate of 10^{-7} dpa·s⁻¹. Defect accumulation inside grains and in grain boundaries is simulated using spatially resolved stochastic cluster dynamics (SRSCD). Using this methodology, sensitivity studies investigating vacancy accumulation in grain boundaries, sink efficiency η of grain boundaries, and vacancy cluster profiles inside grains are performed by varying model input parameters such as defect migration and binding energies inside grain boundaries. Principal component analysis of these model input parameters is then carried out to identify which defect behaviors are strongly correlated with changes in damage accumulation metrics when varying many parameters at once. In both of these analyses, single vacancy and self-interstitial diffusion inside grain boundaries, small vacancy cluster diffusion inside grain boundaries, and the binding energy of vacancies and self-interstitials to grain boundaries are shown to have the greatest impact on defect accumulation.

Keywords: cluster dynamics, grain boundary, radiation damage, sink efficiency

1. Introduction

Materials in nuclear reactors are exposed to extreme environments including high radiation doses and temperatures [1–6]. In structural metals, radiation damage causes the formation of point defects such as vacancies and self-interstitial atoms (SIAs), as well as clusters of these defects such as voids, dislocation loops, and stacking fault tetrahedra [7–15]. These defects in turn can cause macroscopic degradation of material properties, such as swelling, hardening, embrittlement, and affect the creep response of the material [15–21]. The development of radiation-resistant materials that minimize these effects is a central issue in the future development of Generation IV and fusion nuclear reactors [4, 22–25].

One approach for the development of radiation-resistant materials is to engineer microstructures that enhance radiation defect recombination, allowing irradiated materials to ‘self-heal’ and therefore minimize deterioration of mechanical properties. Grain boundaries and bi-material

interfaces can act as recombination sites for point defects, thereby reducing the amount of radiation damage in an irradiated metal [26, 27]. Several types of advanced materials have been developed with this property in mind for potential use in nuclear environments, such as oxide dispersion-strengthened (ODS) steels [24, 25], nanoscale laminate materials [28, 29], nanoporous metals [30, 31], and nanocrystalline metals [32, 33]. For example, ultra-fine grained Fe-Cr-Ni alloys implanted at room temperature with helium ions to a peak concentration of 4 at.% and total damage of 5.5 dpa show an approximate 50% decrease in helium bubble density, 30% decrease in helium bubble size, and 50% decrease in hardening compared to coarse-grained Fe-Cr-Ni alloys [32]. All of these materials have a high interface surface area to volume ratio compared to bulk metals, and show increased resistance to radiation damage.

The ability of grain boundaries to act as efficient and unbiased sinks for both vacancies and self-interstitials significantly impacts the radiation tolerance of nanocrystalline metals. Experiments of defect accumulation and defect denuded zone formation in the vicinity of grain bound-

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aries have shown a dependence on grain boundary character [34–37]. Denuded zone widths have thus been hypothesized to be dependent on the sink efficiencies of various grain boundaries [34], although sink efficiency bias between vacancies and interstitials is not investigated in these experiments. At the atomic scale, grain boundary sink efficiency has been investigated by predicting the binding energies of single vacancies and SIAs to a variety of different grain boundaries [38, 39]. However, the length and time scales of such simulations are too small to simulate defect accumulation in the grain interior or inside grain boundaries, making comparisons between such modeling efforts and experimental results challenging.

To address the shortcomings of the above methods, multi-scale modeling tools are necessary to bridge the gap between atomic-scale studies of grain boundary-defect interactions and experimental evidence of grain boundary-dependent radiation damage tolerance. Several methods for modeling radiation defect accumulation over larger time and length scales have been developed for such a purpose, including cluster dynamics (CD) and object kinetic Monte Carlo (OKMC) [40–47] methods. These tools use values of defect binding and migration energies derived from atomic-scale simulations as inputs, and allow simulation of radiation doses and defect concentrations that are large enough to compare directly to experiments that employ techniques such as transmission electron microscopy (TEM) and positron annihilation spectroscopy (PAS) [43–47]. However, defect migration and binding energies in grain boundaries are still largely unknown and are difficult to characterize using atomistic methods for many materials and grain boundary types. As a result, multi-scale simulations that use atomic-scale predictions of defect energetics as inputs are typically limited to bulk materials or thin films [43–51].

In order to extend multi-scale modeling efforts to complex materials such as nano-grained metals, a wide range of information describing defect properties and behaviors inside grain boundaries is needed. Atomistic studies investigating a limited set of grain boundaries have obtained some defect migration energies for several metals [39, 52–55], and multi-scale studies using OKMC have been implemented for limited cases using atomistic predictions of binding and migration energies as inputs [39]. However, defect behaviors in grain boundaries depend on the specific atomic scale structure of the material interface (misorientation, defect content, etc.) such that a comprehensive quantification of these variables is not amenable to atomistic scale simulations. Therefore, it is important to identify the defect behaviors within grain boundaries that have the greatest impact on damage accumulation, in order to inform future atomic-scale studies.

In this work, spatially resolved stochastic cluster dynamics (SRSCD), a multi-scale radiation damage accumulation tool [56], is applied to the problem of radiation damage accumulation in nanocrystalline α -Fe near grain boundaries. In order to identify key parameters governing

defect accumulation, defect migration and binding energies are varied for each defect type present in the boundary. The impact of varying these energies is measured using three metrics: (1) the density and size of vacancy clusters that accumulate inside the grain boundary, (2) the sink efficiency of the grain boundary for both vacancies and self-interstitials (SIAs), and (3) the profile of vacancy clusters in the grain interior as a function of distance from the grain boundary. These sensitivity analyses are first carried out by changing two variables at a time inside the grain boundary, in order to identify regimes of damage accumulation that can occur near grain boundaries ranging from damage suppression to amplification of vacancy cluster formation. Next, a multivariate statistical analysis is used to investigate correlations between grain boundary variables and damage accumulation metrics when many defect behaviors are changed simultaneously.

The manuscript is organized as follows. In Section 2, a list of physical parameters used as input into SRSCD is presented. Known parameters in bulk α -Fe such as defect binding and migration energies are listed and a list of the various grain boundary parameters tested in this study is given. Section 3 describes the simulation procedure employed in this study, including a description of SRSCD and the geometry of the simulated grain and grain boundary. Results for the dependence of damage accumulation on material parameters are given in Section 4. First, results of a sensitivity analysis of the various parameters governing defect behaviors inside the grain boundary are discussed in Section 4.1, including migration and binding energies of point defects and clusters. Second, results of a sensitivity analysis of the binding of defects to the grain boundary are discussed in section 4.2. Finally, the impact of changing allowed defect behaviors in the simulation such as cluster emission by the grain boundary is investigated in Section 4.3. In Section 5, a statistical analysis of the various grain boundary parameters is used to identify correlations between defect behaviors and damage accumulation metrics when many defect behaviors are changed simultaneously. Discussion of results and conclusions are presented in Sections 5 and 6.

2. Defect behaviors and energetics in the grain interior and in grain boundaries

In this section, the physical model used to simulate damage accumulation in bulk α -Fe and in grain boundaries is presented. This model includes a set of defects expected in such a system, along with their allowed behaviors and the energetics governing their binding and migration.

2.1. Defect behaviors and energetics in bulk α -Fe

The defects modeled in the grain interior are:

1. *Single defects:* these are self-interstitial atoms (SIA) or vacancies (V). These defects migrate in three dimensions and can cluster or annihilate with other defects [40, 57].

2. *Vacancy clusters*: these are treated as spherical clusters in SRSCD. Small vacancy clusters (size 2-4) are mobile in three dimensions [57] and can cluster and annihilate with self-interstitial atoms. Larger vacancy clusters are treated as immobile, but can still interact with other mobile defects. Single vacancies can dissociate from vacancy clusters of all sizes.
3. *Small self-interstitial clusters (size 2-4)*: these SIA clusters migrate in three dimensions [57] and are treated as spherical clusters in SRSCD.
4. *Larger mobile self-interstitial clusters*: these defects are treated as circular dislocation loops which diffuse in one dimension along their Burgers vector [58]. Diffusion of larger SIA clusters between volume elements cannot be restricted to a single crystallographic diffusion direction due to the mean-field formulation of SRSCD. However, their reaction rates for interaction with other defects reflect one dimensional migration and circular geometry [59].
5. *Larger immobile self-interstitial clusters*: these SIA clusters are formed when two mobile SIA clusters meet and form a junction [60] or a mobile SIA cluster encounters a trap. In SRSCD, these defects are treated as immobile circular clusters.

The diffusivity and binding energies of the various defect types listed here are taken from ab-initio and atomistic simulations [57, 58] and are listed in Table 1. These inputs have been used in previous SRSCD simulations which have successfully reproduced experimental results for damage accumulation in neutron-irradiated coarse-grained iron [59]. A list of the allowed reactions such as clustering, dissociation, and diffusion and associated reactions rates for defect behavior in bulk α -Fe used in this work can also be found in [59].

2.2. Defect behaviors and energetics in grain boundaries

Unlike in bulk α -Fe, defect behaviors and energetics in α -Fe grain boundaries have not been predicted in sufficient detail using ab-initio or atomistic techniques. Defect diffusivities depend on migration energies E_m , which represent energetic barriers for defect motion and are typically treated using an Arrhenius relationship:

$$D = D_0 e^{-\frac{E_m}{k_b T}} \quad (1)$$

where D_0 is a diffusion prefactor determined by the attempt frequency for diffusion, typically on the order of $8 \times 10^{11} \text{ nm}^2\text{s}^{-1}$ [57], k_b is Boltzmann's constant, and T is the absolute temperature. Due to the exponential relationship between migration energy and diffusivity, small changes in E_m can affect diffusivity by several orders of magnitude. Molecular dynamics (MD) studies using the empirical Johnson potential [61] have estimated that in symmetric $\Sigma 5(210)[001]$ (36.9°) tilt boundaries, the migration energy for vacancies is 0.51 eV while self-interstitial migration energies are at least 1.26 eV [52, 53], rendering them essentially immobile at room temperature due to

the Arrhenius relationship described above. This contrasts with migration energies in the grain interior of 0.67 eV for vacancies and 0.34 eV for self-interstitials [57], indicating accelerated vacancy diffusion but decelerated interstitial diffusion in these boundaries. This result is qualitatively similar to results for point defect diffusivity in some Cu boundaries [54], although intra-grain boundary diffusivity is expected to be dependent on the grain boundary character and the concentration of defects in the grain boundary.

Due to the unknown nature of various defect energetics inside grain boundaries, in this study all allowed reactions and energetics not treated as free variables inside the grain boundary during a given set of simulations are set as equal to their values in bulk α -Fe unless otherwise noted. An exception to this rule is that all vacancy and SIA clusters inside the grain boundary are assumed to be spherical, unlike large SIA clusters in the grain interior which are assumed to form dislocation loops. In addition, large SIA clusters (greater than 4 SIAs) inside the grain boundary are assumed to be immobile.

The following defect properties are treated as variables inside the grain boundary and their impact on defect accumulation is tested through sensitivity analyses in Section 4:

1. The migration energy E_m of single vacancies and single SIAs inside grain boundaries
2. The migration energy E_m of small (size 2-4) vacancy and SIA clusters inside grain boundaries
3. The binding energy E_b of a single vacancy to a vacancy cluster or a single SIA to an SIA cluster inside grain boundaries
4. The binding energy E_b of single vacancies and SIAs to the grain boundary

3. Methodology

3.1. SRSCD: description

A brief overview of SRSCD is presented here. The central idea of SRSCD is to solve concentration rate equations from mean field rate theory stochastically inside a finite volume element. Rate equations for the time evolution of the concentration of defects $\frac{dC}{dt}$ are typically in the form:

$$\frac{dC}{dt} = \nabla \cdot [D \cdot \nabla C] + f(\mathbf{x}, t), \quad (2)$$

where $f(\mathbf{x}, t)$ is a source term including the reaction rates for all defect-defect interactions as well as creation and trapping at sinks. Reaction rates for allowed reactions such as clustering, diffusion, and dissociation are based on mean-field approximations and are derived from the work of others [40, 62, 63].

Given an element with volume V , if the concentration of defects in the volume is C (in atomic fraction), then the total number of defects in that volume is $N = \frac{CV}{\Omega}$ where V is the volume of the simulated volume element

Migration parameters	$D = D_0 e^{-\frac{E_m}{k_b T}}$	
Single vacancy	$E_m = 0.67$ eV, $D_0 = 8.2 \times 10^{11}$ nm ² /s	[57]
2- <i>v</i> cluster	$E_m = 0.62$ eV, $D_0 = 8.2 \times 10^{11}$ nm ² /s	[57]
3- <i>v</i> cluster	$E_m = 0.35$ eV, $D_0 = 8.2 \times 10^{11}$ nm ² /s	[57]
4- <i>v</i> cluster	$E_m = 0.48$ eV, $D_0 = 8.2 \times 10^{11}$ nm ² /s	[57]
Larger <i>v</i> clusters	(immobile)	
Single interstitial	$E_m = 0.34$ eV, $D_0 = 8.2 \times 10^{11}$ nm ² /s	[57]
2- <i>i</i> cluster	$E_m = 0.42$ eV, $D_0 = 8.2 \times 10^{11}$ nm ² /s	[57]
3- <i>i</i> cluster	$E_m = 0.43$ eV, $D_0 = 8.2 \times 10^{11}$ nm ² /s	[57]
4- <i>i</i> cluster	$E_m = 0.43$ eV, $D_0 = 8.2 \times 10^{11}$ nm ² /s	[57]
<i>n</i> - <i>i</i> cluster (1D)	$E_m = .06 + .11(n^{-1.6})$, $D_0 = (3.5 \times 10^{10} + 1.7 \times 10^{11} n^{-1.7})$ nm ² /s	[58]
Binding energies		
V ₂ → V+V	$E_b = 0.3$ eV	[57]
V ₃ → V ₂ +V	$E_b = 0.37$ eV	[57]
V ₄ → V ₃ +V	$E_b = 0.62$ eV	[57]
Vacancy clusters ($n > 4$)	$E_b^v(n) = 2.07 - 3.01(n^{\frac{2}{3}} - (n-1)^{\frac{2}{3}})$	[57]
I ₂ → I+I	$E_b = 0.8$ eV	[57]
I ₃ → I ₂ +I	$E_b = 0.92$ eV	[57]
Interstitial clusters ($n > 3$)	$E_b^i(n) = 3.77 - 5.05(n^{\frac{2}{3}} - (n-1)^{\frac{2}{3}})$	[57]

Table 1: Migration and binding parameters for vacancies and self-interstitials in bulk α -Fe.

and Ω is the atomic volume. In SRSCD, N is treated as an integer value and reaction rates for defects not present in the volume are not calculated. The reaction rates for any two defects to combine or any one defect to dissociate from a cluster are thus found by converting reaction rates taken from rate theory to rates for a finite volume element by multiplying them by $\frac{V}{\Omega}$. Using this method, all reaction rates are converted to finite-volume rates with units s^{-1} . A derivation of the reaction rates used in this work can be found in [56] and in Appendix A for reactions on the grain boundary. As an example, the reaction rate (in s^{-1}) for clustering between two vacancy cluster types i and j with n_i and n_j vacancies in each cluster inside a volume element containing N_i and N_j clusters of each type (where N is treated as an integer value) is given by [56]:

$$\text{reaction rate} = \omega(n_i^{\frac{1}{3}} + n_j^{\frac{1}{3}})(D_i + D_j)N_i N_j \frac{\Omega}{V} \quad (3)$$

where V is the volume of the element, Ω is the atomic volume, D_i and D_j are the diffusivities of each cluster type, and ω is a geometric constant. The term $\omega(n_i^{\frac{1}{3}} + n_j^{\frac{1}{3}})$ represents the reaction distance required for two spherical defects to interact. Modifications to this functional form for reaction rate occur based on the geometry of the defects (circular dislocation loops rather than spherical clusters) and the dimensionality of diffusivity of the defects, which can cause reaction rates that are quadratic in N_i or N_j [64].

Due to the use of reaction rates from mean-field rate theory, SRSCD treats defects as homogeneously distributed within volume elements and therefore does not allow spatial resolution below the scale of the volume elements used in a given simulation [59]. This method contrasts with

other kMC-based methods for simulating radiation damage accumulation such as object kinetic Monte Carlo (OKMC) [40, 57, 65], in which defects with specified coordinates diffuse within a simulation volume and are allowed to interact only when they come within a pre-determined reaction distance of each other.

In order to evolve the defect populations in an irradiated material in a stochastic way, allowed reactions are chosen and time is iterated according to the classic kinetic Monte Carlo (kMC) algorithm, instead of using a standard deterministic time integration scheme as in the case of rate theory. It has been demonstrated [63] that this approach correctly solves the master equation for the time evolution of the entire system.

In this work, the synchronous parallel kinetic Monte Carlo algorithm of Martínez et al. [66] is used in order to increase the size of the simulated domain. In a parallel simulation, the simulation volume is divided among several processors. To apply the kinetic Monte Carlo algorithm, the simulation is advanced in time stochastically by choosing random numbers r_1 and $r_2^d \in (0, 1)$, with $d \in [1, D]$ in a simulation with D total processors. A single time step is then chosen for all processors while a separate reaction is chosen inside processor d using random number r_2^d , according to the formula:

$$\tau = \frac{1}{a_{\max}} \ln \left(\frac{1}{r_1} \right), \quad \sum_{\nu=0}^{\mu-1} a_{\nu}^d < r_2^d a_{\max} \leq \sum_{\nu=0}^{\mu} a_{\nu}^d, \quad (4)$$

where a_{ν}^d is the reaction rate of reaction ν inside processor d and $a_{\max}$ is the maximum of the total reaction rates a^d

inside each processor:

$$a^d = \sum_{\mu=1}^M a_{\mu}^d, \quad a_{\max} = \max_d \{a^d\} \quad (5)$$

After each timestep, the numbers of defects in the relevant volume elements are updated for each defect type involved in the reaction chosen. The reaction rates for all relevant reactions are subsequently updated and this process is repeated until the system has evolved for a pre-determined amount of time. A derivation of the serial KMC algorithm can be found in [63], while the parallel KMC algorithm can be found in [66]. Use of the synchronous parallel SRSCD method has been shown not to significantly impact damage accumulation results [67], and therefore the number of processors used in the following simulations is not reported. A detailed discussion of the computational methodology used in this work is presented in [56] and [67].

3.2. Simulating grain boundaries in SRSCD

In the following sections, SRSCD is used to simulate uniform Frenkel pair implantation in nanocrystalline α -Fe, including the effect of grain boundary trapping and re-emission of defects. In the proposed approach, the geometry considered is as follows: the grain and grain boundary system is approximated by a simulation volume that is 100 nm thick in the x -direction and infinite in the y and z -directions. The size of the total simulated volume is 105 nm $\times$ 50 nm $\times$ 50 nm, so that the grain is 100 nm thick and the boundary is represented by one additional layer of volume elements. All volume elements are 5 nm in length and periodic boundary conditions are applied in all directions, as shown in Figure 1. Therefore, only a single grain boundary is modeled, as periodic boundary conditions allow it to capture defects diffusing in both the $+x$ and $-x$ directions.

Allowed reactions and reaction rates inside the grain interior are the same as in previous studies, and can be found elsewhere [67]. As defect diffusion inside the grain boundary is assumed to be two dimensional, reaction rates for defect clustering and diffusion between elements while inside the grain boundary are altered. The functional form for the reaction rate for defect clustering and annihilation is computed using the same method as three dimensional clustering rates [56, 62], and can be found in Appendix A.

A defect trapping and emission model for grain boundaries is implemented in this work in order to investigate the impact of grain boundary parameters on defect accumulation and sink efficiency. Defects are allowed to migrate from the grain into the grain boundary using a reaction rate that treats the grain boundary as a perfect sink for defects diffusing from the bulk, regardless of the concentration of defects inside the grain boundary. However, defect emission from the grain boundary is allowed for single vacancies and single self-interstitials. The reaction rate used

Figure 1: Two dimensional schematic of layout of SRSCD simulations. The grain is simulated with a 100 nm thin film using 5 nm volume elements (white), with a grain boundary acting as a barrier in the $+x$ -direction (gray). All boundary conditions are periodic, so that diffusion in the $-x$ -direction also leads to trapping on the grain boundary. Defect trapping and emission from the grain boundary are depicted with colored arrows.

for vacancy or SIA emission from the grain boundaries is the same as the reaction rate used for point defect dissociation from defect clusters [56]:

$$\text{reaction rate} = \omega D_{V,I} e^{-\frac{E_b(V,I)}{k_b T}} N_{V,I} \quad (6)$$

where ω is a geometric constant, $E_b(V,I)$ is the binding energy of vacancies or SIAs to the grain boundary, $N_{V,I}$ is the number of vacancies or SIAs inside the grain boundary element, and $D_{V,I}$ is the diffusivity of vacancies or SIAs inside the grain. The diffusivity of point defects in bulk α -Fe rather than inside the grain boundary is used here because the total energy required for emission from the grain boundary is equal to the binding energy to the grain boundary plus the energy required to move the defect one additional diffusive step away from the boundary. Since this final step is taken within the grain, $D_{V,I}$ is taken to be the diffusivity in the grain interior.

Grain boundaries are therefore not perfect sinks in this work, and instead have a sink efficiency η defined as the probability that a defect trapped in the grain boundary will remain in the grain boundary. The probability that a defect will be emitted from the grain boundary is given by the ratio of the number of defects emitted from the grain boundary N_{emit} to the number of defects trapped at the grain boundary N_{trap} . Therefore η is given by:

$$\eta = 1 - \frac{N_{\text{emit}}}{N_{\text{trap}}} \quad (7)$$

Using this formulation, a grain boundary with sink efficiency $\eta = 0$ will not trap any defects, while a grain boundary with sink efficiency $\eta = 1$ will trap all defects that diffuse towards it and will act as a perfect sink. This sink efficiency depends on the grain boundary binding energy as well as many other factors, such as the implantation conditions and the allowed defects and reactions between defects in the grain boundary. In addition, the

sink efficiencies for vacancies and self-interstitials, η_V and η_I , are in general not equal. In Sections 4.2 and 4.3, values for sink efficiency are reported along with populations of defects in the grain boundary and in the grain interior for the irradiation conditions investigated here. It should be noted that due to the implantation conditions and allowed defects chosen in this study, a steady-state defect population is not achieved during irradiation. Therefore, sink efficiencies η_V and η_I reported in Section 4.2 and 4.3 may change as a function of irradiation dose.

In all simulations in this study, Frenkel pairs are implanted uniformly into the grain at room temperature to a total dose of $10^{-3} - 10^{-2}$ dpa and at a dose rate of 10^{-7} dpa·s $^{-1}$. This dose rate was chosen to maximize the fraction of vacancies that reach the grain boundary as single vacancies rather than small mobile clusters. This rate corresponds to dose rates in neutron irradiation experiments [15, 68], although displacement cascades formed during neutron irradiation are not considered here. The populations of SIA clusters are not reported in the results of this work because the concentrations of these defects are very low in the simulation results. This is mainly due to their fast diffusivity in the grain interior as well as the fact that all defects are initially introduced as Frenkel pairs, so the formation of large dislocation loops is unlikely.

4. Impact of grain boundary defect energetics on damage accumulation

In order to investigate the impact of the various defect behaviors listed in Section 2.2 on damage accumulation in the vicinity of the grain boundary, several sensitivity analyses are performed in this section. The goal of these analyses is to find, within a limited input space, regimes in which different trends for defect accumulation can be observed. In Section 4.1, defect behaviors inside the grain boundary are varied while leaving the binding energies of defects to the grain boundary constant. The parameters varied in this section are point defect and cluster migration energies (Sections 4.1.1 and 4.1.2) and the binding energies of point defects to clusters within the grain boundary (Section 4.1.3). In Section 4.2, the effect of changing the binding energy of vacancies and SIAs to the grain boundary is investigated. Finally, in Section 4.3, the potential impact of cluster emission from the boundaries on defect accumulation within this system is studied. As a reference, Table 2 shows the various grain boundary properties varied throughout this section.

4.1. Defect binding and diffusion inside grain boundaries

In this section, SRSCD is used to simulate Frenkel pair implantation as described in Section 3.2 to a total dose of 10^{-3} dpa. The metrics used to quantify the impact of changing various defect behaviors in this section are the concentration of vacancies and vacancy clusters inside the grain boundary (in units of atomic fraction) and the

average size of vacancy clusters inside the grain boundary. In all simulations in this section, vacancies are assumed bound to the grain boundary with energy $E_b = 0.26$ eV and self-interstitials are assumed bound to the grain boundary with energy $E_b = 1.29$ eV, corresponding to the average defect binding energies in a $\Sigma 5$ grain boundary [38]. This choice was made because the mobility of defects inside this grain boundary has been investigated in atomistic simulations [52, 53] and it represents an intermediate case for point defect binding to the grain boundary, as studied by Tschopp et al. [38].

4.1.1. Single vacancy and SIA mobility

Figure 2 shows the vacancy concentration (in atomic fraction) and average vacancy cluster size inside the grain boundary as a function of single vacancy and SIA migration energies E_m inside the grain boundary. The migration energies E_m for point defect diffusivity in the grain interior (0.67 eV for vacancies and 0.34 eV for SIAs) as well as the values predicted by atomistic results inside $\Sigma 5$ grain boundaries [52, 53] (0.51 eV for vacancies and 1.26 eV for SIAs) are indicated on Figure 2 with + symbols as a reference. Note that in Figure 2b, some local variations in average cluster size are seen in regions where the vacancy concentration is low due to poor statistics in these regions. This is demonstrated in Figure 2c, where the standard deviation in average vacancy cluster size for five simulations at each value of $E_m(V)$ and $E_m(SIA)$ is shown. The standard deviation is seen to be higher where the average concentration of vacancies is low, contributing to the inhomogeneity in Figure 2b.

The results shown in Figure 2 can be divided roughly into four quadrants, which represent different regimes of defect accumulation:

1. For low values of vacancy migration energy $E_m(V)$ and self-interstitial migration energy $E_m(SIA)$, both single vacancies and single self-interstitials are very mobile within the grain boundary. In this case, a low number of vacancies remain inside the grain boundary at the end of the simulation due to annihilation between the two defect types.
2. For low values of $E_m(V)$ but high values of $E_m(SIA)$, vacancies are mobile but self-interstitials are relatively immobile. In this case, vacancies either annihilate with self-interstitials or form larger, immobile clusters. Therefore the density of vacancy clusters is low but the average size is high in this quadrant.
3. For high values of $E_m(V)$ and low values of $E_m(SIA)$, immobile vacancies and mobile self-interstitials create a regime of intermediate vacancy content but very low average vacancy cluster size in the grain boundary.
4. For high values of both $E_m(V)$ and $E_m(SIA)$, neither defect type is mobile inside the grain boundary and thus very little interaction between vacancies and self-interstitials occurs. In this case, a large

Quantity varied	Range	Section
Point defect migration energies	$E_m(\text{V})$ 0.3 – 1 eV $E_m(\text{SIA})$ 0.2 – 1.3 eV	4.1.1
Cluster migration energies	$E_m(\text{V clusters})$ 0.2 – 1 eV $E_m(\text{SIA clusters})$ 0.2 – 1.3 eV	4.1.2
Parameter A in cluster binding energies (see equation (8))	$A(\text{V clusters})$ 0.3 – 3.9 eV $A(\text{SIA clusters})$ 0.8 – 4.4 eV	4.1.3
Point defect - grain boundary binding energies	$E_b(\text{V})$ 0 – 1.2 eV $E_b(\text{SIA})$ 0 – 2.5 eV	4.2
Cluster - grain boundary binding energies	$E_b(\text{V clusters})$ 0 – 1.2 eV $E_b(\text{SIA clusters})$ 0 – 2.5 eV	4.3

Table 2: Grain boundary properties varied in sensitivity analyses carried out in this section

concentration of single vacancies is trapped in the grain boundary but the average size is low.

Overall, the migration energies of single vacancies and self-interstitials inside the grain boundary both have strong impacts on defect accumulation inside the grain boundary. Therefore, predicting these values using atomistic methods is important in designing models to accurately simulate radiation damage in the vicinity of various grain boundaries.

4.1.2. Defect cluster mobility

The growth and annihilation of defect clusters depends on the mobility of point defects (treated in the previous section) as well as small defect clusters. Therefore, in this section the diffusivities of small clusters of vacancies and SIAs (size 2-4) inside the grain boundary are also investigated while leaving single vacancy and SIA migration energies constant. Due to the large number of parameters that could be independently varied in such a study, the migration energies of vacancy clusters size 2-4 are set to the same value and varied together. The migration energy of SIA clusters size 2-4 is varied in the same way. Results showing vacancy concentration inside the grain boundary as a function of cluster migration energies within the grain boundary are shown in Figure 3. Two cases for single defect migration energies were chosen, corresponding to the + symbols in Figure 2: In Figure 3a, single V and SIA migration energies are 0.51 and 1.26 eV, respectively, corresponding to atomistic results for $\Sigma 5$ boundaries [52, 53]. In Figure 3b, single vacancy and SIA diffusion is the same as in bulk α -Fe. The average size of vacancy clusters inside the grain boundary was also investigated but is not shown in Figure 3 as results were relatively constant for both cases studied here.

The migration energy of small vacancy clusters strongly influences the vacancy concentration predicted by SRSCD on the grain boundary above 0.7 eV, but the migration energy of SIA clusters is a less significant variable here. This is due to the fact that such SIA clusters are relatively rare on the grain boundary in these simulations.

4.1.3. Defect cluster binding energy

Finally, the competition between defect cluster growth by capture of mobile defects and dissociation of point defects from clusters can play a role in defect accumulation. The stability of defect clusters is a function of the binding energy E_b of point defects to those clusters, which represents the energetic barrier for emission of a point defect from a cluster within the grain boundary. The effect of changing the binding energy for dissociation of vacancy and self-interstitial clusters inside the grain boundary is also investigated. Note that this energy represents the energy barrier for point defect emission from a defect cluster while remaining inside the boundary, rather than the binding energy of those defects to the boundary itself. As a first approximation, we assume that the binding energy of defects to clusters size n inside the grain boundary follows the same law as in the grain interior, given by a functional form [57]:

$$E_b(n) = A + (B - A) \left[\frac{n^{\frac{2}{3}} - (n-1)^{\frac{2}{3}}}{2^{\frac{2}{3}} - 1} \right] \quad (8)$$

where A and B are constants representing the limiting binding energy as $n \rightarrow \infty$ and the binding energy when $n = 2$, respectively. The effect of changing parameter A is investigated here, with B equal to 0.3 eV for vacancies and 0.8 eV for SIAs, the values for 2-V and 2-SIA binding energies inside the grains (see Table 1). The impact of parameter A in equation (8) on the binding energy of a vacancy cluster size n is shown in Figure 4. Note that in bulk α -Fe, values for binding energies of small vacancy (size 2-4) and SIA (size 2-3) clusters are given separately from the functional form of equation (8), but in this parameter study the functional form is applied to clusters of all sizes inside the grain boundary.

Average vacancy cluster sizes are shown in Figure 5 for the same two cases of vacancy and SIA diffusion inside the grain boundary shown in Figure 3. As in Figure 2b, some statistical variation in cluster sizes is seen in Figure 5 due to low overall vacancy concentration. However, it is still possible to identify regions of different defect accumulation due to different grain boundary defect binding energies. For the case of $E_m(\text{V}) = 0.51$ eV and

(a)

(b)

(c)

Figure 2: Grain boundary vacancy concentration (2a) and average cluster size (2b) for several different values of migration energies $E_m(V)$ and $E_m(SIA)$ inside the grain boundary. Marked points represent the V and SIA migration energies in bulk (0.67 and 0.34 eV, respectively [57]) and on $\Sigma 5$ grain boundaries (0.51 and 1.26 eV, respectively [52, 53]). The standard deviation of average vacancy cluster sizes computed over five simulations is shown in (2c).

(a)

(b)

Figure 3: Grain boundary vacancy concentration for several different interfacial values of cluster migration energy. (3a) Single vacancy and SIA migration energies are fixed at 0.51 eV and 1.26 eV, respectively, in accordance with atomistic simulations of $\Sigma 5$ grain boundaries [52, 53]. (3b) Single vacancy and SIA migration energies are fixed at 0.67 eV and 0.34 eV, respectively, their values in bulk α -Fe [57].

Figure 4: Effect of parameter A in equation (8) on the binding energy $E_b(V)$ of a single vacancy to a vacancy cluster size n , with parameter $B = 0.3$ eV.

$E_m(\text{SIA}) = 1.26$ eV, parameter A in vacancy cluster binding energy is significant below $A = 1$ eV, with decreasing cluster size as A decreases. For the case of $E_m(V) = 0.67$ eV and $E_m(\text{SIA}) = 0.34$ eV, parameter A in vacancy cluster binding energy is significant below $A = 0.5$ eV, causing decreasing cluster size as A decreases. The average concentration of vacancy clusters inside the grain boundary was also investigated but is not shown in Figure 5 as results were relatively constant for both cases studied here.

4.2. Binding energy of point defects to grain boundaries

In this section, the ability of grain boundaries to act as efficient sinks for radiation-induced defects is investigated as a function of $E_b(V)$ and $E_b(\text{SIA})$, the binding energy of vacancies and SIAs to the grain boundary. Three types of results are obtained here: (1) vacancy concentration and average size inside the grain boundaries, (2) grain boundary sink efficiency for both vacancies and self-interstitials, and (3) the profile of vacancy clusters in the interior of the grain. Using these three measures, a more complete picture of defect accumulation at and near grain boundaries is obtained for a variety of different grain boundary behaviors.

The binding energies of single vacancies and SIAs to grain boundaries in α -Fe have been investigated by Tschopp et al. using atomistic simulation techniques [38]. Although these binding energies are not uniform throughout the grain boundary, their averages have been computed for a range of common grain boundaries as well as twist and asymmetric tilt grain boundaries. As a guide for the reader, these values are overlaid on the results shown in this section. Clearly, the various other defect behaviors have not been parameterized on each of these grain boundaries and therefore these results are meant to serve as a qualitative guide rather than predictions for defect accumulation in specific grain boundaries. Therefore, the results of this section can be interpreted as investigating one

Figure 5: Grain boundary average cluster size for several different interfacial values of A in equation (8). (5a) Single vacancy and SIA migration energies are fixed at 0.51 eV and 1.26 eV, respectively, in accordance with atomistic simulations of $\Sigma 5$ grain boundaries [52, 53]. (5b) Single vacancy and SIA migration energies are fixed at 0.67 eV and 0.34 eV, respectively, their values in bulk α -Fe [57].

aspect of changing grain boundary character, while leaving other parameters such as defect diffusivity constant. These results demonstrate the range of binding energies of point defects to grain boundaries and the resulting different regimes of damage accumulation that could be expected in a real material.

To study the effect of binding energies E_b to the grain boundary, uniform Frenkel pair implantation in the grain interior is simulated with irradiation conditions as described in Section 3.2. All results are shown for a total dose of 10^{-3} dpa. Vacancy and SIA migration energies inside the grain boundary in these simulations are given by $E_m(V) = 0.51$ eV and $E_m(SIA) = 1.26$ eV, similar to atomistic results for $\Sigma 5$ grain boundaries [52, 53]. Results of this sensitivity study are shown in Figure 6. Although not shown here, results analogous to those shown in Figure 6 were also obtained for the case of $E_m(V) = 0.67$ eV and $E_m(SIA) = 0.34$ eV, their values in bulk α -Fe (similar to Figures 3 and 5). These results do not change the qualitative analysis of the impact of point defect binding energies to grain boundaries on defect accumulation, and are therefore not included here. In Figures 6a and 6b, the vacancy concentration and average size, respectively, are shown on the grain boundary as a function of $E_b(V)$ and $E_b(SIA)$. Both vacancy concentration and average size on the grain boundary are strongly dependent on $E_b(V)$ and $E_b(SIA)$. To better understand the mechanisms behind defect accumulation, Figures 6c and 6d show the sink efficiencies η_V and η_I as a function of the same binding energies $E_b(V)$ and $E_b(SIA)$. Together these maps of defect accumulation and sink efficiency can be roughly divided into four regions:

1. $E_b(V) < 0.2$, $E_b(SIA) < 0.5$: In this region, neither vacancies nor SIAs are strongly bound to the grain boundary and η_V and η_I are nearly zero. However, a few immobile vacancy clusters are trapped on the grain boundary. Therefore, the concentration of vacancies on the grain boundary is very low, but the vacancy clusters that are trapped on the grain boundary are large.
2. $E_b(V) > 0.2$, $E_b(SIA) < 0.5$: In this region, vacancies are trapped by the grain boundary but SIAs are not, giving $\eta_V \simeq 1$ and $\eta_I \simeq 0$. Therefore, the boundary accumulates a surplus of vacancies, although the size of clusters found on the boundary is smaller than in the first region. Note that none of the grain boundaries studied by Tschopp et al. [38] fall into this region.
3. $E_b(V) < 0.2$, $E_b(SIA) > 0.5$: In this region, vacancies are not strongly bound to the grain boundary, with $\eta_V < 1$ but SIAs are strongly bound, with $\eta_I \simeq 1$. Therefore, there is a surplus of SIAs on the grain boundaries and both the size and concentration of vacancy clusters on the grain boundary is very small.
4. $E_b(V) > 0.2$, $E_b(SIA) > 0.5$: In this region, both vacancies and self-interstitials are strongly trapped by the grain boundary and $\eta_V \simeq \eta_I \simeq 1$. In this region,

vacancies tend to form clusters in the grain boundary because of their greater diffusivity relative to that of SIAs inside the grain boundary. However, the average size of vacancy clusters on these grain boundaries is still small compared to the first region.

The results of Tschopp et al. [38], overlaid on Figures 6a-6d, indicate that a wide range of grain boundary behaviors could be expected in the vicinity of a grain boundary, as a wide range of binding energies of defects to grain boundaries have been found in atomistic results. Although these points are not intended to simulate actual grain boundary behavior due to the lack of knowledge of other parameters, they are used to choose some points lying within regions 1, 3, and 4 listed above for which the vacancy cluster profiles inside the grain interior can be investigated. These points are indicated with numbers in Figure 6a. The vacancy cluster profiles created using these binding energies are shown in Figures 6e and 6f at a higher dose of 10^{-2} dpa along with the vacancy cluster profiles created using two limiting cases: (1) a 100 nm thin film with free surfaces that act as perfect sinks and (2) a bulk medium with no grain boundaries and periodic boundary conditions in all directions.

For the sake of illustration, we choose several points in Figure 6a, indicated by numbers 1-5, to investigate defect accumulation within the grain interior. Anecdotally, points 1-5 correspond to the binding energies of vacancies and self-interstitials to $\Sigma 3$, $\Sigma 5$, $\Sigma 9$, $\Sigma 11$, and $\Sigma 13a$ grain boundaries found in the work of Tschopp et al. [38], respectively. The defect profiles and average sizes shown in Figures 6e and 6f show a variety of different damage accumulation trends, depending on which region listed above the grain boundary binding energies $E_b(V)$ and $E_b(SIA)$ fall into:

1. For case 1, the grain interior is almost completely defect-free. This is due to the slight bias of the grain boundary to trap vacancy clusters, and contradicts experimental observations of coherent twin boundaries [34, 69]. This difference may be explained by grain boundary emission of small vacancy clusters, as discussed in Section 4.3.
2. For cases 2 and 5, the grain boundary is biased towards trapping self-interstitials, and the resulting surplus of vacancies in the grain interior leads to the opposite effect. In this case, both the average vacancy concentration and size are higher than for the case of a system with no grain boundaries.
3. For cases 3 and 4, both vacancies and SIAs are trapped on the grain boundary and the defect accumulation profile resembles that of a perfect sink.

These results indicate that the effects of grain boundaries on defect accumulation can vary widely, with behaviors ranging from strong suppression of defect formation inside some grains to amplification of vacancy cluster formation inside others. Therefore, the binding energies

Figure 6: Maps of void concentration (6a), average size (6b), and sink efficiencies η_V (6c) and η_I (6d) on the grain boundary as a function of binding energy of vacancies and self-interstitials to the grain boundary, at a total dose of 10^{-3} dpa. Marked points indicate average binding energies of defects to grain boundaries found by Tschopp et al. [38]. (6e and 6f) Profiles showing vacancy cluster concentration and average size inside the bulk for several chosen values of E_b (V) and E_b (SIA), corresponding to values for specific grain boundaries found by Tschopp et al. [38].

$E_b(V)$ and $E_b(SIA)$ of defects to grain boundaries are primary variables necessary for correctly modeling defect accumulation in a nanocrystalline metal, in agreement with Uberuaga et al. [39] Note that no correlation between grain boundary binding energy and misorientation angle is observed in the results of Tschopp et al. [38]

4.3. Cluster emission from grain boundaries

For case 1 in Figure 6e, the defect profile inside the grain is in qualitative disagreement with experimental results. In this case, grain boundary binding energies for single vacancies and self-interstitials corresponding to the $\Sigma 3[110]$ grain boundary [38] are found to cause decreased vacancy accumulation inside the grain. This contrasts with experiments in helium-irradiated copper [34, 69] and quenched gold [36], in which defect accumulation near twin boundaries proceeded as if the boundary was not present, indicating a low sink efficiency for defects. Indeed, the sink efficiency η_V for vacancies in this grain boundary as shown in Figure 6c is on the order of 10^{-3} . However, the sink efficiency η_I for self-interstitials in this grain boundary is on the order of 10^{-5} , even lower than η_V . Therefore, there is a slight surplus of SIAs in the grain interior, causing annihilation of the majority of vacancies and vacancy clusters and decreasing the defect concentration in the grain. This behavior was found to persist even when decreasing the values of $E_b(V)$ and $E_b(SIA)$ to 0 eV.

The discrepancy between these results and experimental results is likely due to the need for inclusion of additional defect behaviors in the model, such as defect cluster emission from the grain boundary. In Sections 4.1 and 4.2, sensitivity analyses are used to investigate the variability in defect accumulation caused by different migration and binding energies of defects in the grain boundary while keeping the allowed defect behaviors and reactions the same. However, this model is based on assumptions such as the ability of the grain boundary to emit only single vacancies and SIAs, rather than clusters of such defects. To demonstrate the necessity of identifying the correct defect behaviors that should be included in such a model, the analysis of Section 4.2 is repeated here while allowing all vacancy and SIA clusters size 1-4 to dissociate from the grain boundary and move back into the bulk with the same binding energy $E_b(V)$ and $E_b(SIA)$. Results of this analysis are shown in Figure 7. When comparing results to Figure 6, results show several significant differences including no vacancy cluster formation on the grain boundary at very low binding energies, a broader Region 3 (described in Section 4.2 above), and a smoother transition from Region 1 to Region 2.

Defect accumulation in the grain interior after irradiation to a higher dose of 10^{-2} dpa, shown in Figures 7e and 7f, is also shown to change significantly as a result of changing the allowed reactions in the system. Overall, using this model, higher populations of vacancy clusters are present in the grain interior and their average sizes are greater when compared to the results of the previous model

shown in Figures 6e and 6f. Importantly, the qualitative disagreement with experiments of damage accumulation near twin boundaries described above is smaller for case 1 in Figure 7e than in Figure 6e and disappears entirely for values of $E_b(V) < 0.1$ eV.

This analysis indicates that for certain grain boundaries such as $\Sigma 3$ boundaries, the ability for defect clusters to emit from the boundary may be a critical factor in predicting their impact on damage accumulation. This phenomenon has not been investigated extensively in atomistic studies of binding energies of defects to grain boundaries [38, 39].

5. Discussion

Although the results presented in the previous sections do not represent predictions for specific grain boundaries, some qualitative comparisons with experimental studies of radiation damage near grain boundaries can be made. Experiments of grain boundary-dependent damage accumulation have focused on defect denuded zones near grain boundaries, usually in FCC metals [34, 36, 69]. These studies have demonstrated that the width of void denuded zones, and thus the sink efficiency of grain boundaries for defects, depends on the grain boundary character.

The results of this study cannot be directly compared to experimental measures of denuded zone width in irradiated α -Fe due to the different material and much lower irradiation dose simulated here ($10^{-3} - 10^{-2}$ dpa) than in typical irradiation experiments (> 1 dpa). However, the shape of the vacancy profile in Figures 6e and 7e can give some insight into whether or not denuded zones are expected near various grain boundaries. Grain boundaries that mimic perfect sinks, such as the cases with binding energies corresponding to $\Sigma 9[110]$ and $\Sigma 11[110]$ boundaries shown in Figure 6e, should result in void denuded zones due to the decrease in vacancy cluster concentration near grain boundaries observed in Figure 6e and 7e. By contrast, grain boundaries that are imperfect sinks for vacancies such as the cases with binding energies corresponding to $\Sigma 5[100]$ and $\Sigma 13a[100]$ boundaries shown in Figure 6e have greater vacancy cluster concentration and size than even the case of a material with no grain boundaries, indicating that denuded zone formation is unlikely for these boundaries. Therefore, the experimentally observed sensitivity of void denuded zone formation to grain boundary character is reproduced in this study, although specific predictions cannot be made without further parameters from atomic-scale simulations. A notable exception is the case of $\Sigma 3$ grain boundaries, as discussed in Section 4.3.

In Section 4, maps of damage accumulation and sink efficiency are shown for two-point correlation studies of binding and migration energies governing defect behavior on grain boundaries. All binding and migration energies not varied in these studies are set to constant values, typically their values in bulk α -Fe. Therefore, the results presented in Section 4 do not describe the full range of possible

Figure 7: Maps of void concentration (7a), average size (7b), and sink efficiencies η_V (7c) and η_I (7d) on the grain boundary as a function of binding energy of vacancies and self-interstitials to the grain boundary, at a total dose of 10^{-3} dpa. Marked points indicate average binding energies of defects to grain boundaries found by Tschopp et al. [38]. (7e and 7f) Profiles showing vacancy cluster concentration and average size inside the bulk for several chosen values of $E_b(V)$ and $E_b(SIA)$, corresponding to values for specific grain boundaries found by Tschopp et al. [38].

defect accumulation behaviors due to the high number of parameters that can be varied inside the grain boundary. A complete description of defect accumulation made by varying all identified parameters simultaneously would be daunting, but a statistical description of the correlation between input and output variables can be made. Therefore, in this section a more complete statistical analysis of the correlations between defect migration and binding energies and the resulting defect accumulation is performed while varying many defect properties simultaneously.

The same eight variables governing defect behavior inside the grain boundary that are investigated in Sections 4.1 and 4.2 are chosen as free variables here: single defect migration energies $E_m(\text{V})$ and $E_m(\text{SIA})$, small defect cluster migration energies $E_m(\text{V Cluster})$ and $E_m(\text{SIA Cluster})$, binding energies of single defects to the grain boundary $E_b(\text{V})$ and $E_b(\text{SIA})$, and parameters $A(\text{V})$ and $A(\text{SIA})$ in the functional form for defect cluster binding energies. Bounds for each variable can be found in Table 2. A total of 3000 sets of these input values are chosen randomly, assuming a uniform probability distribution and domains for each variable given by the same domains tested in in Section 4. Irradiation is simulated to a total dose of 10^{-3} dpa at room temperature, as described in Section 3.2. The following metrics are used to probe potential statistical correlations using the eight input variables described above: vacancy concentration in the grain boundary $C(\text{V})$, average vacancy cluster size in the grain boundary, and sink efficiencies η_V and η_I . Five simulations are run for each set of input variables and average values of output variables are computed. Note that the goal of this analysis is to investigate correlations between input and output variables, rather than between input variables which are uncorrelated due to their random choice. Clearly, correlations do exist between binding and migration energies of defects inside grain boundaries, such as the inverse correlation between $E_m(\text{V})$ and $E_m(\text{SIA})$ in grain boundaries observed by Uberuaga et al. [39], but these relationships are not investigated here.

Using the eight variables governing defect behavior and four metrics used to measure defect accumulation provided by these simulations, a $n \times m$ matrix X of data points is constructed ($n = 3000$ and $m = 8 + 4 = 12$ here), with x_{ij} representing the value of input or output variable j obtained in dataset i . This matrix is then converted into a deviation matrix D , in which d_{ij} is given by:

$$d_{ij} = \frac{x_{ij} - \overline{x_j}}{\sigma_{x_j}} \quad (9)$$

where $\overline{x_j}$ is the average value of variable j over all datasets and σ_{x_j} is the standard deviation of variable j over all datasets. Next, the $m \times m$ correlation matrix R is computed which provides the correlation between all input and output variables tested here. R is given by:

$$R = \frac{1}{n} D^T \cdot D \quad (10)$$

Thus, the value for correlation r_{ij} between any two variables i and j is:

$$r_{ij} = \frac{d_{ki}d_{kj}}{n} \quad (11)$$

using the Einstein convention to imply a sum over k . This is the standard definition of correlation. A description of the methodology used to find R can be found in ref. [70]. As the correlations between input variables are zero due to their random choice, the subset of R showing correlations between either one input and one output variable or two output variables is shown in Table 3. Correlation values range between -1 and 1 , indicating perfect inversely and perfect directly correlated variables, respectively.

Defect behaviors that are strongly correlated with changes in damage accumulation are necessary for accurate simulation of defect evolution in nanocrystalline systems. The strongest correlations found between input and output variables are between the binding energies of single defects to the grain boundary $E_b(\text{V})$ and $E_b(\text{SIA})$ and the corresponding sink efficiencies η_V and η_I , at 0.724 and 0.763 for vacancies and SIAs, respectively. A strong correlation is also seen between the migration energy of single vacancies $E_m(\text{V})$ and the concentration and average size of vacancies in the grain boundary, at 0.501 and -0.216 , respectively. Input parameters with low correlations to output variables are $E_m(\text{SIA clusters})$ and cluster binding energy parameters $A(\text{V})$ and $A(\text{SIA})$. The metrics used to measure defect accumulation are also shown to be correlated in this analysis. A positive correlation exists between grain boundary vacancy concentration $C(\text{V})$ and sink efficiency η_V , and both of these variables are inversely correlated to average vacancy cluster size. In addition, self-interstitial sink efficiency η_I is inversely correlated to average vacancy cluster size on the grain boundary, although η_I is not strongly correlated to the other output variables.

To test the convergence of the analysis performed in this section, the eigenvalues λ_k of the correlation matrix R are shown in Figure 8 as a function of the number of sets of input parameters used to generate them. These results show that the values for λ_k and by extension the correlation between the various input and output parameters has converged once 3000 sets of inputs have been generated.

Overall, the results of this section are in agreement with the results presented in Section 4, indicating that the most important parameters necessary for simulating radiation defect accumulation in nano-grained $\alpha\text{-Fe}$ are $E_m(\text{V})$, $E_m(\text{SIA})$, $E_b(\text{V})$, and $E_b(\text{SIA})$. Note that these results are dependent on the irradiation conditions chosen. For the irradiation conditions chosen in this study, the majority of defects arriving at the grain boundary are single vacancies and SIAs. During cascade damage or at higher dose rates, the impact of cluster behavior at the grain boundary could be more significant.

The correlations described in this section give relationships between individual defect behaviors and damage accumulation in nanocrystalline $\alpha\text{-Fe}$. However, it is also

Correlation matrix

	$C(V)$	Size(V)	η_V	η_I
$E_m(V)$	0.501026775	-0.216087858	-0.158020377	1.29×10^{-2}
$E_m(SIA)$	0.147239909	0.145007676	-2.73×10^{-3}	-5.93×10^{-2}
$E_m(V \text{ Clusters})$	0.142412381	-0.138616306	2.10×10^{-2}	7.29×10^{-4}
$E_m(SIA \text{ Clusters})$	3.42×10^{-2}	4.74×10^{-2}	2.21×10^{-2}	-1.97×10^{-2}
$E_b(V)$	0.207899832	-0.140550804	0.723818559	-1.05×10^{-2}
$E_b(SIA)$	5.27×10^{-2}	-0.23088202	5.42×10^{-2}	0.762664155
$A(V)$	-3.28×10^{-2}	2.27×10^{-2}	-7.96×10^{-3}	-7.15×10^{-2}
$A(SIA)$	2.59×10^{-3}	-7.07×10^{-3}	-1.41×10^{-2}	1.20×10^{-3}
$C(V)$	1	-0.193738479	0.212013526	6.61×10^{-2}
Size(V)	-0.193738479	1	-0.210381828	-0.312326674
η_V	0.212013526	-0.210381828	1	9.21×10^{-2}
η_I	6.61×10^{-2}	-0.312326674	9.21×10^{-2}	1

Table 3: Correlations between defect binding and migration energies in grain boundaries and metrics for damage accumulation in simulations of Frenkel pair irradiation of nanocrystalline α -Fe, using simulation parameters given in Section 3.2. All correlation results are reported in the range $[-1, 1]$

Figure 8: Progression of eigenvalues λ of the correlation matrix as a function of the number of data points used. The data set shows convergence once 3000 sets of inputs have been generated.

useful to investigate groups of variables that frequently vary together, in order to develop a physical understanding of the processes that drive defect accumulation inside grain boundaries. This analysis is given in Appendix B using principal component analysis.

6. Conclusions

In this study, a novel scheme for investigating the impact of grain boundary-dependent parameters on defect accumulation in α -Fe with 100 nm grains is implemented using spatially resolved stochastic cluster dynamics (SRSCD). Defect diffusion within grains is treated using three dimensional reaction rates in SRSCD, while defect diffusion and clustering within grain boundaries is treated using two dimensional reaction rates in SRSCD. Grain boundaries are treated as imperfect sinks by applying boundary condi-

tions between the grain interior and the grain boundary associated with perfect sinks but allowing thermal emission of point defects from grain boundaries into the grain interior with a binding energy that is treated as a parameter. Using this scheme, three types of results are used to investigate the influence of grain boundaries on defect accumulation: (1) vacancy concentration and average size inside the grain boundaries, (2) grain boundary sink efficiency η_V and η_I for vacancies and SIAs, respectively, and (3) the resulting profile of immobile vacancy clusters inside the grains as a function of distance from the grain boundary.

Sensitivity analyses are used to investigate which defect behaviors inside grain boundaries are the most important in governing defect accumulation in and near grain boundaries. Variables identified as having the greatest influence on defect accumulation results are single vacancy and SIA diffusivity inside grain boundaries and the binding energy of vacancies and SIAs to grain boundaries. Vacancy cluster diffusivity inside grain boundaries is also shown to be significant but has a smaller impact on defect accumulation. Variables such as SIA cluster diffusivity inside grain boundaries and the binding energy of point defects to vacancy and SIA clusters inside grain boundaries are shown to be of lesser importance. In addition, emission of defect clusters rather than single defects is shown to have a significant impact on defect accumulation. Statistical analysis of the results of 3000 randomly chosen sets of input parameters is also performed in order to identify trends in the variance of defect accumulation results when varying many defect behaviors in the grain boundary at once. The results of this analysis agree with the results of the sensitivity studies in identifying the most important parameters to quantify in order to accurately simulate defect accumulation in and near grain boundaries.

The analyses performed in this work are intended to guide future atomistic studies of defect behaviors in grain

boundaries. The results presented here indicate that, in order to create reliable multi-scale models of defect accumulation in irradiated nanocrystalline metals, point defect migration energies inside grain boundaries and point defect binding energies to grain boundaries need to be characterized as a function of grain boundary character and defect content. In addition, these results indicate that cluster emission from grain boundaries is a necessary component of multi-scale models of damage accumulation near low-angle grain boundaries such as $\Sigma 3$ boundaries. Once these parameters have been characterized, the methodology presented in this work can be used to simulate defect evolution near specific grain boundaries and compare results to experimental measures of defect accumulation such as void denuded zones and grain boundary void formation.

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Appendix A. Derivation of 2D sink strengths

In this section, a derivation of the reaction rate for defects diffusing on a two-dimensional surface will be given. The goal of this formulation is to homogenize the spatially resolved problem of defects diffusing and becoming trapped at fixed sinks. Therefore, we consider two concentration rate equations $c_e(t)$ and $c_h(t)$, the exact and homogeneous distributions of a given defect type, respectively. Assuming a constant rate of implantation K (in units of defects·m⁻²s⁻¹), the rate equations for the population evolution of these two formulations for concentra-

Figure A.9: Schematic of the domain used in this section to derive sink strength k^2 of a sink in a two-dimensional plane. Spatially resolved concentration field $c_e(r, t)$ is solved explicitly using boundary conditions at $r = r_s$ and $r = r_o$. Homogeneous concentration $c_h(t)$ is set equal to $c_e(r = r_o, t)$ at steady-state.

tion are:

$$\frac{dc_e}{dt} = K + D\nabla^2 c_e, \quad \frac{dc_h}{dt} = K - Dk_s^2 c_h \quad (\text{A.1})$$

The rate equation for c_e uses boundary conditions to treat the impact of sinks, while c_h uses a homogenized sink strength term k_s^2 to treat the presence of sinks. Therefore, k^2 is found by solving the rate equation for c_e explicitly around a single sink and setting the concentrations c_e and c_h equal.

The solution to $\frac{dc_e}{dt}$ is found in a two-dimensional surface around a circular sink with radius r_s inside a circular area with outer radius r_o . A schematic of the layout used in this derivation is shown in Figure A.9. The value of r_o is chosen such that the area A enclosed by r_o , given by $A = \pi r_o^2$, is the inverse of the concentration of sinks in the global medium, $c_s = \frac{1}{\pi r_o^2}$. Assuming cylindrical symmetry, the spatial derivatives simplify to:

$$\frac{dc_e}{dt} = K + D \left(\frac{1}{r} \frac{d}{dr} r \frac{dc_e}{dr} \right) \quad (\text{A.2})$$

which has steady-state ($\frac{dc_e}{dt} = 0$) solution given by:

$$c_e(r) = \alpha_1 \ln(r) + \alpha_2 - \frac{Kr^2}{4D} \quad (\text{A.3})$$

where α_1 and α_2 are integration constants. By imposing the boundary conditions $c_e(r_s) = 0$ and $\frac{dc_e}{dr}(r_o) = 0$, this equation simplifies to:

$$c_e(r) = \frac{K}{4D} \left[2r_o^2 \ln\left(\frac{r}{r_s}\right) + (r_s^2 - r^2) \right] \quad (\text{A.4})$$

The steady-state solution to $\frac{dc_h}{dt} = 0$ is given by $c_h = \frac{K}{Dk_s^2}$. To solve for k^2 , the concentration $c_e(r_o)$ is set equal to c_h , giving:

$$k_s^2 = \frac{4}{2r_o^2 \ln\left(\frac{r_o}{r_s}\right) + (r_s^2 - r_o^2)} \quad (\text{A.5})$$

Substituting $c_s = \frac{1}{\pi r_o^2}$, this simplifies to:

$$k_s^2 = \frac{4\pi c_s}{2 \ln\left(\frac{r_o}{r_s}\right) + \left(\frac{r_s^2}{r_o^2} - 1\right)} \quad (\text{A.6})$$

To simplify this equation, we require that $r_o \gg r_s$, allowing the second term in the denominator to be neglected, giving:

$$k_s^2 = \frac{4\pi c_s}{2 \ln\left(\frac{r_o}{r_s}\right) - 1} \quad (\text{A.7})$$

Substituting the sink strength k_s^2 into $\frac{dc_h}{dt}$ in equation (A.1), we get the following rate equation for the evolution of the population of defects in a homogeneous medium with sinks:

$$\frac{dc_h}{dt} = K - \frac{4\pi D c_s c_h}{2 \ln\left(\frac{r_o}{r_s}\right) - 1} \quad (\text{A.8})$$

Noting again that $c_s = \frac{1}{\pi r_o^2}$, this equation can be expressed as a function of c_s , c_h , and r_s :

$$\frac{dc_h}{dt} = K - \frac{4\pi D c_s c_h}{2 \ln\left(\sqrt{\frac{1}{\pi c_s r_s^2}}\right) - 1} \quad (\text{A.9})$$

In typical mean field rate theory problems, instead of treating one defect type in a concentration field of sinks, we typically simulate two or more types of defects, each acting as a sink for the other defects. Therefore, in a model two-species system of vacancies and self-interstitials, c_v and c_i , with a reaction distance r and diffusivities D_v and D_i , the total equation for the evolution of the system is given by:

$$\begin{aligned} \frac{dc_v}{dt} &= K_v - \frac{4\pi D_v c_v c_i}{2 \ln\left(\sqrt{\frac{1}{\pi c_i r^2}}\right) - 1} - \frac{4\pi D_i c_v c_i}{2 \ln\left(\sqrt{\frac{1}{\pi c_v r^2}}\right) - 1} \\ \frac{dc_i}{dt} &= K_i - \frac{4\pi D_v c_v c_i}{2 \ln\left(\sqrt{\frac{1}{\pi c_i r^2}}\right) - 1} - \frac{4\pi D_i c_v c_i}{2 \ln\left(\sqrt{\frac{1}{\pi c_v r^2}}\right) - 1} \end{aligned} \quad (\text{A.10})$$

Note that in equation (A.10), two terms are added to each rate equation - one representing the rate of vacancy diffusion and capture by stationary self-interstitials, and one representing mobile self-interstitial diffusion and capture by stationary vacancies. This method assumes that, when both defect types are mobile, the reaction rate for interaction between mobile defects can be deconvoluted into two reaction rates in which one defect type is mobile and one defect type is stationary.

Figure A.10: Comparison of mean field rate theory and two-dimensional OKMC simulation of point defect diffusion and annihilation using the 2D reaction rate given in equation (A.10). Defect diffusivities are taken from values for single vacancies and self-interstitials in α -Fe at three different temperatures.

The validity of the model presented in equation (A.10) is investigated here by comparison with a 2D OKMC simulation including single vacancies and single interstitials. The only allowed reactions in the OKMC simulation are implantation, diffusion, and annihilation when two defects come within a reaction radius of each other. All parameters are the same in the OKMC and MFRT simulations. Using a single implantation rate $K_v = K_i = K$, the population of vacancies and interstitials as a function of total dose is compared at three different temperatures (yielding different diffusivities D_v and D_i) between OKMC and MFRT simulations. Figure A.10 shows these results. Both steady-state and transient populations show a good fit between OKMC and MFRT simulations.

As described in [56], the rate equations (A.10) are converted to units of s^{-1} and the reaction rate for interaction between two defect types i and j used in SRSCD is given by:

$$\text{reaction rate (s}^{-1}\text{)} = \frac{4\pi N_i N_j}{A} \times \left[\frac{D_i}{2 \ln \left(\sqrt{\frac{A}{\pi N_j}} \left(\frac{1}{r_i + r_j} \right) \right) - 1} + \frac{D_j}{2 \ln \left(\sqrt{\frac{A}{\pi N_i}} \left(\frac{1}{r_i + r_j} \right) \right) - 1} \right] \quad (\text{A.11})$$

where N_i , N_j , D_i , and D_j are the numbers of defects type i and j and their diffusivities, respectively, inside the grain boundary element in SRSCD. A is the area of the grain boundary element. The values r_i and r_j are the radii of each defect type, given by

$$r_i = \left(\frac{3n_i\Omega}{4\pi} \right)^{\frac{1}{3}} \quad (\text{A.12})$$

such that $r_i + r_j$ is the reaction distance between the two

defects. The value n_i is the number of vacancies or interstitials making up defect type i . This approximation assumes that, although the defects diffuse in a two-dimensional surface, they still take the form of spheres.

Appendix B. Principal component analysis

In this appendix, principal component analysis [70, 71] is performed in order to identify the sets of variables that most strongly influence damage accumulation. The eigenvectors v_k of the correlation matrix R shown in Table 3 are the principal components of the system. The first principal component v_1 represents the direction in m dimensional space along which the value of $v_{1j}d_{ij}$ has maximum variance, for $i \in [1, n]$. The second principal component v_2 is then defined as the direction orthogonal to v_1 with maximum variance of $v_{2j}d_{ij}$, and so on. The variance of principal component v_k is given by λ_k , the eigenvalue of that eigenvector. Frequently, the majority of the variance in the system can be accounted for by only a few principal components, allowing analysis of the most important relationships between variables. Table B.4 shows the principal components of R most responsible for variation in the output variables. Communality between the principal components and the output variables is also given in Table B.4b. The communality between variable j and component v_k is the percentage of the variation in d_{ij} accounted for by principal component v_k . This analysis shows that between 77 – 87% of the variation in each of the four output variables is explained by the first four principal components. All of the principal components v_k , variances λ_k , and values of communality for output variables are given in Appendix C.

To better understand the relationships between defect behaviors and damage accumulation, the principal components are converted to $\tilde{v}_k = \lambda_k^{\frac{1}{2}} v_k$. In this form, the value of $\tilde{v}_{kj}$ represents the correlation between variable j and principal component k [71]. These values are then plotted for each variable j using two principal components at a time on circles of correlation [70], as shown in Figure B.11. The closer a variable is to the edge of a circle of correlations, the greater percentage of variation in that variable can be explained by those two principal components. By contrast, variables near the center of the circle are less important for those two components. These circles of correlation are used as a visual tool to describe the variables in each principle component as well as their relative significance due to the variance λ of the principal component. By visually inspecting Figure B.11, the following observations can be made:

1. In Figure B.11a, the first principal component indicates an inverse correlation between the size of vacancy clusters and $E_m(V)$, $E_b(V)$, $E_b(\text{SIA})$, $C(V)$, η_V , and η_I . This is expected, as an increase in vacancy concentration, decrease in vacancy cluster size, and increase in sink efficiency for both vacancies and

Input variables	PC ₁	PC ₂	PC ₃	PC ₄
$E_m(V)$	0.189648805	-9.10×10^{-3}	0.663954208	-0.10918847
$E_m(SIA)$	-3.38×10^{-2}	-8.24×10^{-2}	0.172736756	0.427359208
$E_m(V \text{ Clusters})$	0.113690271	-4.69×10^{-2}	0.162400282	-0.162878248
$E_m(SIA \text{ Clusters})$	-1.34×10^{-2}	-5.53×10^{-2}	2.30×10^{-3}	0.13985207
$E_b(V)$	0.347789213	-0.522657117	-0.239754004	-0.134593369
$E_b(SIA)$	0.411961479	0.478592409	-0.155900304	-0.205989958
$A(V)$	-7.24×10^{-2}	-6.00×10^{-2}	-2.03×10^{-2}	-5.11×10^{-2}
$A(SIA)$	3.92×10^{-3}	2.13×10^{-2}	7.84×10^{-2}	-3.41×10^{-2}
Output variables				
$C(V)$	0.344511533	-0.215825353	0.511062898	-0.26503984
Size(V)	-0.42956806	-7.02×10^{-2}	-9.23×10^{-2}	-0.78054255
η_V	0.390880624	-0.460214683	-0.341264526	-1.33×10^{-2}
η_I	0.444807211	0.46722243	-0.168630532	-0.123915238
Variance (λ_k)	2.154309427	1.740299394	1.505798711	0.650006163

(a) Principal components

	PC ₁	PC ₂	PC ₃	PC ₄
$C(V)$	0.255691100	0.081064160	0.393292466	0.045660409
Size(V)	0.397531957	0.008567315	0.012835851	0.396014092
η_V	0.329151901	0.368591156	0.175367541	0.000115532
η_I	0.426237563	0.379901788	0.042819278	0.009980836

(b) Communality

Table B.4: (B.4a) The four eigenvectors of the correlation matrix R most responsible for the variance in the output variables, referred to a principal components. Variance in $v_{kj}d_{ij}$, for $i \in [1, 3000]$, is given by λ_k . (B.4b) Communality values between output variables and principal components. Communality indicates the percentage of variation in each output variable that is explained by a given principal component.

1. SIAs occurs when vacancies and self-interstitials are more strongly bound to and less mobile inside the grain boundary.
2. In Figure B.11a, the second principal component indicates that when $E_b(SIA)$ is inversely correlated with $E_b(V)$, η_I is inversely correlated with η_V and $C(V)$ as well. This result is also expected, as an increase in binding energy for one defect type accompanied by a decrease in binding energy of another defect type leads to biased trapping of the defect type with the higher binding energy by the grain boundary.
3. In Figure B.11b, the third principal component indicates that $E_m(V)$ and $C(V)$ are inversely correlated with η_V and to a lesser extent η_I , $E_b(V)$, and $E_b(SIA)$. This corresponds to the situation in which vacancy clusters are more mobile and simultaneously more tightly bound to the grain boundary, leading to greater sink efficiency but a lower concentration of vacancy clusters due to interactions with other defects (annihilation with interstitials and formation of larger clusters).
4. In Figure B.11b, the fourth principal component indicates an inverse correlation between $E_m(SIA)$ and the size and concentration of vacancy clusters on the grain boundary. This result is surprising, as it indicates that as self-interstitial diffusion slows (increasing migration energy), the concentration and aver-

age size of vacancy clusters in the grain boundary simultaneously decrease. By contrast, in Figure 2 we see that the regions of greatest vacancy concentration and average vacancy cluster size are found when $E_m(SIA)$ is high. Therefore, principal component analysis has enabled identification of a physical result that could not be identified in the two-variable studies of Section 4. This principal component can be interpreted physically as a decrease in SIA mobility causing an increased number of SIAs to act as recombination sites for mobile vacancy clusters inside the grain boundary, thereby decreasing average vacancy cluster sizes. However, it should be noted that the variance of this principal component is $\lambda_4 = 0.650$, indicating that this effect is not as strong as the other effects listed here.

Appendix C. Principal components of the correlation matrix

Table C.5 shows the 12 principal components v_k of the correlation matrix R , their variances λ_k , and the communality associated with each principal component for the output variables. Communality represents the percentage of variation in that output variable that is explained by variation along principal component v_k . The analysis in Section 5 is performed only using principal components 1, 2, 3, and 9 as these four principal components are respon-

Principal Components	PC ₁	PC ₂	PC ₃	PC ₄	PC ₅	PC ₆	PC ₇	PC ₈	PC ₉	PC ₁₀	PC ₁₁	PC ₁₂
<i>E_m</i> (V)	0.189648805	-9.10E-03	0.663954208	-3.41E-02	0.16638697	-4.53E-02	0.25457005	-0.10918847	-0.554913059	-0.215166361	-0.243552339	
<i>E_m</i> (SIA)	-3.38E-02	-8.24E-02	0.172736756	0.7413347	-0.392133851	3.18E-02	0.152732957	-0.176875995	-0.136472162	-4.43E-02	1.96E-02	
<i>E_m</i> (V Clusters)	0.113690271	-4.69E-02	0.162400282	-0.409267345	0.141454574	0.123488651	-0.711384795	-0.162875248	-0.156824657	-5.23E-02	8.24E-03	
<i>E_m</i> (SIA Clusters)	-1.34E-02	-5.53E-02	2.30E-03	8.73E-02	0.33818973	-0.369861724	0.13985207	-4.67E-02	4.23E-03	0.49998237	0.49998237	
<i>E_b</i> (V)	0.347789213	-0.239757117	-0.239754004	5.60E-02	2.55E-02	-2.19E-02	-5.29E-02	5.98E-02	-0.12140714	0.292299164	0.292299164	
<i>E_b</i> (SIA)	0.411961479	-0.478592409	-0.155900304	-0.155900304	-0.112508606	-0.290611111	0.786914047	-0.447196009	-0.205989588	-0.363391917	0.363391917	
<i>A</i> (V)	-7.24E-02	-6.00E-02	7.84E-02	-2.03E-02	-4.23E-02	7.04E-02	8.46E-02	-1.84E-02	-5.11E-02	4.53E-03	1.38E-02	
<i>A</i> (SIA)	3.92E-03	2.13E-02	-0.215825353	0.137317775	0.150134338	0.484484712	-0.805970874	-0.225321525	-3.41E-02	3.678E-02	1.25E-02	
<i>C</i> (V)	0.344511533	-7.02E-02	0.511062898	0.137317775	1.01E-02	-1.81E-03	-1.54E-02	1.68E-02	-0.26503984	0.647981691	0.156849431	
<i>Size</i> (V)	-0.42956806	-0.460214683	-0.341264536	-9.23E-02	-6.86E-03	-3.41E-02	0.102248462	-8.11E-02	-0.78054255	-9.17E-02	-0.136877924	
η_V	0.39080624	0.467222343	-0.341264536	7.28E-02	-1.46E-03	1.16E-02	-2.48E-02	-2.73E-03	-1.33E-02	-0.134325227	-0.368112893	
η_I	0.44807211	0.467222343	-0.168630532	0.124904792	-1.46E-04	4.04E-02	5.83E-02	5.05E-03	-0.123915238	4.87E-03	-0.593272498	
Variance (λ_k)	2.154309427	1.740293934	1.565798711	1.096009155	1.02484058	0.998599854	0.995266691	0.935180852	0.65006163	0.427183943	0.230232414	
Communality	0.256591.1	0.08106416	0.393292466	0.020666536	0.00010483	0.000237184	0.011754851	0.000268479	0.045660409	0.17936611	0.005664119	
<i>C</i> (V)	0.000867315	0.0012835851	0.00158738312	0.0058788317	3.36288E-06	0.001161783	0.010405262	0.000459348	0.0003591109	0.0043195763	0.000509763	
η_V	0.329513901	0.368591156	0.175367341	0.006809047	4.82023E-05	0.000133301	0.000410148	0.000410148	0.000115532	0.001707794	0.031198127	
	0.426237563	0.379901788	0.042819278	0.017099066	2.18566E-08	0.001627554	0.003386127	2.4254E-05	0.009808836	1.0113E-05	0.081035422	

Table C.5: Principal components v_k and variances λ_k of the correlation matrix R (top), and communality of the output variables for each principal component.

(a) Principal components 1 and 2

(b) Principal components 3 and 4

Figure B.11: Circles of correlations between input (blue) and output (red) variables and the first four principal components. Input variables with low correlation to principal components are not labeled.

sible for between 77–87% of the variance in all four output variables.