Title

Kinetic Monte Carlo Modelling of Nano-oxide Precipitation and its Associated Stability under Neutron Irradiation for the Fe-Ti-Y-O system.

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Abstract:

When developing nuclear materials, it is difficult to predict their behavior under decades long irradiation regimes. Machine and deep learning can be very important tools that can help predict material properties. However, these tools require the use of strong and robust models that can carefully reproduce the microstructural evolution against experiments so researchers can understand the material processes and to validate the model for future use with other materials. Thus, a newly developed Kinetic Monte Carlo (KMC) model was constructed to investigate the precipitation behavior of Y-Ti-O oxides along grain boundaries in nanostructured ferritic alloys (NFA) and the oxide response to neutron irradiation. The level of radiation damage simulated reached the long dpa range required for reactor components. Simulations were conducted to investigate the influence of temperature as well as the influence of grain boundary sinks on the resulting oxide characteristics of a 12YWT-like alloy during heat treatments at 1023 K, 1123 K, and 1223 K. There is good agreement of the oxide characteristics from simulation with literature values and the influence of the grain boundary on precipitation is slight. The same oxide
configuration and positions were input into a new simulation and placed under simulated neutron irradiation to a total accumulated dose of 8 dpa at three temperatures, 673 K, 773 K, and 873 K, and at dose rates of $10^{-3}$, $10^{-4}$, and $10^{-5}$ dpa/s. The expected inverse relationship of oxide size with dose rate was observed. A long-term irradiation simulation at 873 K and $10^{-3}$ dpa/s was taken out to 66 dpa and it was found that the oxides in the vicinity of the grain boundary were more susceptible to dissolution. Additionally, irradiation simulations of a 14YWT-like alloy were conducted to replicate findings from neutron irradiation experiments. The larger oxides in the 14YWT-like alloy simulated in the KMC did not dissolve and showed the similar stability as in the experiments.

I. Introduction

The next generation of nuclear fission reactors and aspiring first-generation fusion reactors are being developed to compete with fossil fuel sources and minimize the emission of greenhouse gases into the environment. To improve their economics, these new reactors are being designed with improved fuel efficiency. However, a new material challenge arises because of the requirement for these reactors to operate at higher temperatures and in more intense irradiation environments, which are outside the limits of current reactor materials\(^1\). The concern is that defects, such as point defects, dislocation loops, and helium bubbles introduced through irradiation damage, will embrittle the material and shorten the lifespan of these components\(^2\). To address these concerns, nanostructured ferritic alloys (NFAs) has been studied extensively for use as nuclear fuel cladding in the reactor environment. There are also potential applications for as-of-yet built fusion reactors as material for blanket structures\(^3\).

The defining characteristics of NFAs are a high number density of nano-sized ($\leq 2$ nm) oxide particles embedded into a ferritic matrix. These nano-oxides provide an alternative nucleation site for bubbles of the transmutation He atoms produced during irradiation so that large bubbles of He atoms do not form at the metal grain boundaries where they would substantially embrittle the material. Instead, smaller bubbles form inside the metal grain, which causes less degradation of the material’s properties\(^4\).

Two NFA alloys, 12YW\(T\) and 14YWT, have been simulated, and these alloys have been extensively studied, including the processing conditions required to achieve oxides of a certain size and number density\(^5\-^7\). NFA oxides are typically composed of oxygen and the metal solutes
Y and Ti. The exact structure of these oxides are undetermined but are commonly thought to have the structure $Y_2O_3$, $Y_2TiO_5$, or $Y_2Ti_2O_7$. Processing of NFAs begins with a metal powder mix of all the components with oxygen being introduced via a $Y_2O_3$ compound. The powder mix is then mechanically alloyed to break the $Y_2O_3$ bonds to release oxygen into the solid solution. The solid solution then undergoes a heat treatment through either hot isostatic pressing, hot extrusion, or spark plasma sintering. At this stage, nano-oxides form in the material. Once formed, the oxides display strong thermal stability at high temperatures, showing little coarsening even at temperatures as high as 1273 K. This stability is especially relevant when the materials are planned for service temperatures below 973 K.

Another attractive property of nano-oxides is their resistance to dissolution under intense irradiation, which helps ensure that the material remains in good condition throughout its lifespan. A literature review from Wharry on experimental studies testing the survivability of nano-oxides under intense irradiation found mixed and sometimes contradictory results across the studies. Some studies found that the oxides were stable when irradiated above 873 K, while other studies showed that the oxides became less stable at that same temperature. Many of these discrepancies are attributed to differences in material processing, testing environment, and characterization techniques; thus, more study is required.

There are limited facilities that can produce the high energy neutrons to irradiate material samples for testing, so proton, electron, and ion irradiation is often used as a substitute for neutron irradiation. Ribis found that ion irradiation has a deep impact on the nano-oxide growth during irradiation with radiation induced oxide growth occurring 17-40 times faster than the growth in samples that were neutron irradiated. Swenson also saw differences in the stability of the nano-oxides when irradiated with protons and neutrons with the nano-oxides being more stable under proton irradiation then neutron irradiation. These experiments gained limited insight into the evolution of nano-oxide characteristics over total accumulated dose as most of the irradiation experiments only analyzed the oxides after two or three dosages.

Possible options to solve these problems are the use of machine/deep learning methods and computer models to simulate the irradiation response. The response of materials to irradiation can be simulated using computer models such as mean field rate-theory, molecular dynamics, cluster dynamics, and phase field models. The Kinetic Monte Carlo (KMC) method
has previously been used to simulate precipitation kinetics of alloys such as Fe-Cu\textsuperscript{18} and Fe-Nb-C\textsuperscript{19}. There are also models that simulate the precipitation of Y-O\textsuperscript{20}, Ti-O\textsuperscript{21}, and Y-Ti-O\textsuperscript{22} oxides using KMC under thermal aging.

This study used a newly developed KMC method to model the NFA systems (12 YWT and 14 YWT) under neutron irradiation. The project builds off a prior KMC model that simulates the precipitation of Y-Ti-O oxides in the bulk region of an NFA\textsuperscript{22}. First the presence of a grain boundary was incorporated into the model to provide a sink for the point defects. Then, a method for simulating neutron irradiation was developed for the model. Soisson extended his KMC model to allow for the modeling of electron radiation damage through the introduction of point defects via Frenkel Pair insertion\textsuperscript{23}. Becquart and Vincent incorporated neutron irradiation in their KMC models by inserting cascade debris from molecular dynamics simulations of displacement cascades into the KMC simulation box\textsuperscript{24,25}. Our model simulates the displacement cascade from neutron impact within the simulation box to the end of the cascade. Our code is improved over other KMC models, so it can mimic displacement cascade and radiation damage up to relevant dpa levels.

The end goal of this study is to construct a KMC computer model that can both simulate the precipitation kinetics of the oxides in an Fe-Ti-Y-O system and the response of the oxides to neutron irradiation events inside a reactor. The KMC model was able to simulate neutron irradiation and the resulting cascade of displacements efficiently enough to reach relevant dpas (i.e., those seen in irradiation experiments). The relationship of oxide survivability under conditions such as temperature and dose rate were investigated. Additionally, this study aimed to compare findings regarding precipitation behavior of $Y_2Ti_2O_7$ in the bulk and near a grain boundary, the shape of the oxides produced, and the irradiation response of the system to other irradiation experiments found in the literature.

II. Methods

1. The Material System

The material system is represented in the KMC model similarly to the model constructed by Hin\textsuperscript{20,21} and in a prior study of the Fe-Y-Ti-O precipitation\textsuperscript{26}. This model starts by creating a system of fixed lattice points in a bcc structure for an Fe system. These points are populated by substitutional atoms of the matrix Fe, and the substitutional solutes Y and Ti while the O atoms
exist on a separate octahedral sub-lattice. The unstressed structure of the oxides is different from the bcc Fe matrix and cannot be represented in this set-up. However, the expected size of these oxides is very small and it can be assumed that the small oxides are coherent with the bcc matrix for the purposes of this study.

The point defects required for atomic migration of the substitutional Fe, Y, and Ti - the vacancies and interstitial dumbbells - both exist on the substitutional lattice: the vacancy as a vacant site and the dumbbell as two atoms occupying the same lattice site. For thermodynamic considerations, all interstitial dumbbells are assumed to be oriented in the <110> position since it is the most energetically favored position of the Fe-Fe dumbbell\textsuperscript{27}.

2. KMC Model

The events the KMC model simulates are: point defect generation, vacancy migration, interstitial migration, and interstitialcy migration. The frequency of these events are quantified and given an event frequency $\Gamma_x$ defined as the number of times per second the event is expected to occur. The model tabulates all possible events and finds a total frequency:

$$\Gamma_{Tot} = \sum \Gamma_x$$

At each Monte Carlo step, an event is randomly selected and the amount of time that passes in that step $t_{mcs}$ is the inverse of the total event frequency:

$$t_{mcs} = \frac{1}{\Gamma_{Tot}}$$

Migration of the interstitial dumbbells, recombination of point defects, and the treatment of grain boundary point defect annihilation for the KMC model follows the method laid out by Soisson\textsuperscript{23}. This KMC model has periodic boundary conditions where mobile defects that migrate out of the simulation box emerge at the opposite side. To study the influence of a defect sink on precipitation, a grain boundary is placed inside the simulation box, where the grain boundary is represented as a perfect planer sink that is a single atomic layer wide. During irradiation simulations, defect sinks (like the grain boundaries) and recombination of the vacancy and interstitial dumbbells are primarily responsible for the removal of point defects from the simulation box.
The jump frequencies $\Gamma_x$ for the migration event are tied to the diffusion properties of the defects and can be calculated through the following relationship:

$$\Gamma_x = \nu_{Fe} \times \exp\left(-\frac{E_{mig}}{k_B T}\right)$$  \hspace{1cm} (3)

where $\nu_{Fe}$ is the attempt frequency and $E_{mig}$ is the migration energy. Calculation of the migration energy in the KMC is based on the local atomic environment around the migrating species:

$$E_{mig} = e^{SP} - I_3 - I_4 - I_o - I_{PD}$$  \hspace{1cm} (4)

$$E_{mig} = e^{SP} - \sum_j \varepsilon_{ij}^3 N_j^3 - \sum_j \varepsilon_{ij}^4 N_j^4 - \sum_{n=1,2} \varepsilon_{iO} N_{O}^n - \sum_j \varepsilon_{ij}^3 N_j^3$$  \hspace{1cm} (5)

The term $e^{SP}$ stands for the saddle-point energy and is constant regardless of any changes in local composition. Other models only use the first nearest neighbors of the solute atom and point defect when calculating the migration energy, denoted as $I_3$ and $I_{PD}$. However, in hopes of greater accuracy, our model includes the 2$^{nd}$ nearest neighbor, denoted as $I_4$. Another addition to previous models is the inclusion of interactions of atoms on different sub-lattices as the atom is migrating, denoted as $I_o$. Eq. 4 is rewritten into Eq. 5 to replace the placeholder terms $I_x$ with their actual terms. $N_j^n$ is the number of $n$ nearest neighbors of species $j$ that the migrating atom $i$ has. For example, $N_Y^3$ is the number of $Y$ atoms in the third nearest neighbor position that the migrating atom $i$ has. The $\varepsilon_{XY}$ terms are the pair-interactions of solutes XY at the nearest neighbor distances ordered 1-4 in the simple cubic system. The 3$^{rd}$ and 4$^{th}$ nearest neighbors is the simple cubic correspond to the 1$^{st}$ and 2$^{nd}$ nearest neighbors in the bcc system. The oxygen atoms migrate through a similar mechanism except that the migration is visualized to be the oxygen atom hopping to an adjacent empty octahedral site. Unlike mean-field rate theory, where interaction with the local environment is averaged, the specific atomic configuration around the migrating species is known. Through this consideration of the local environment, we can see effects such as binding more easily. It also allows for the formation of clusters that lead to precipitation.

The parameterization is given in Sections II.3 and II.4.

3. Parameterization

This section provides details of the thermodynamic and kinetic parameterization of the Fe-Ti-Y-O system.
Table 1 lists the pair-interaction energies used to describe the Fe-Ti-Y-O system from 1st to 4th nearest neighbors in the simple cubic system. The model extends parameterization performed in a prior precipitation study\textsuperscript{26} by adding interstitial dumbbell interactions. Pair-interaction energies between all the constituent elements are found through a procedure described in Hin’s model\textsuperscript{20} using a mixture of experimental and calculated material property values such as the defect formation energy, solubility limits, and solubility products. The pair-interactions for yttrium and titanium with a dumbbell was taken from the energies of formation of the <110> dumbbell when the solute atom was in one of its first-nearest neighbor positions\textsuperscript{27}.

A second critical aspect for the accuracy of the model is tying the kinetics of the system to the diffusion properties of each solute in the Fe system. The system is set so that each solute in pure bcc metal reproduces the diffusion values from the literature or experiments, the background is described in a prior paper simulating the same material \textsuperscript{26}. Table 2 lists the diffusional values critical to the system.

| Input Parameter | Value | Unit | Reference |
|-----------------|-------|------|-----------|
| lattice parameter | 2.87 x 10^{10} | m | |
| Vacancy Migration Energy, Fe | 0.66 | eV | \textsuperscript{20} |
| Vacancy Migration Energy, Y | 0.23 | eV | \textsuperscript{28} |
| Vacancy Migration Energy, Ti | 0.81 | eV | \textsuperscript{21} |
|Interstitial Migration Energy, Fe | 0.35 | eV | \textsuperscript{23} |
|Interstitial Migration Energy, Y | 0.21 | eV | calculated |
Interstitial Migration Energy, Ti 0.24 eV calculated
Vacancy Formation Energy 2.24 eV 20
Oxygen Migration Energy 0.48 eV 29
Vacancy pre-exponential factor, Fe 6.0x10^-4 m^2/s 20
Vacancy pre-exponential factor, Y 3.7x10^-7 m^2/s 28
Vacancy pre-exponential factor, Ti 2.1x10^-1 m^2/s 21
Interstitial pre-exponential factor, Fe 1.0x10^-5 m^2/s
Interstitial pre-exponential factor, Y 1.0x10^-5 m^2/s
Interstitial pre-exponential factor, Ti 1.0x10^-5 m^2/s
Interstitial attempt frequency 1.0x10^14 /s

Table 2 Diffusion parameters for the Fe-Ti-Y-O system

4. Treatment of the Grain Boundary

At the grain boundary (simulated here as a perfectly planar sink), energy exists from the imperfections at the boundary. This energy makes it more or less preferable for particular solutes to segregate at the grain boundary. Each solute species has a certain segregation energy that is added to the calculation of the migration energy while the solute is in the plane of the grain boundary. There is a slight temperature dependence of the segregation energies given by the entropy. These values are listed in table 3.

| Atomic Species | ΔH       | AS          |
|----------------|----------|-------------|
| O              | 0.9984 eV| 4.784x10^-4 eV/K |
| Ti             | 0.3328 eV| 3.016x10^-4 eV/K |
| Y              | 0.6448 eV| 6.552x10^-4 eV/K |

Table 3 Segregation enthalpy and entropy of selected solutes in bcc Fe

The O and Ti segregation values are from values calculated by Lejcek and the Y segregation values were found for this study from the solubility limit of Y in bcc Fe using Lejcek’s method. Each of the solutes are assumed to be encountering a general type grain boundary. The KMC model treats the segregation as such: when solute atoms are present on the same plane as the grain boundary, the segregation energies are added to the migration energies calculated in Eq. 5. This either repulses the solute or inhibits the solute’s departure from the grain boundary and on the large scale potentially results in the enrichment or depletion of that solute’s atomic species at the grain boundary.

5. Neutron Irradiation
The primary source of damage during irradiation is from the impact of high energy neutrons with metal atoms in the material. The collision creates a cascade of displacements, which introduces defects into the material such as vacancies and interstitial dumbbells. Neutrons emitted from the nuclear reactions in the fuel are expected to have energies in the 0.1 MeV to 10 MeV range\textsuperscript{31}. To simulate the neutron impact, we start with the assumption that the neutron has an energy of 1 MeV. The neutron strikes a random substitutional site in the matrix and is assumed, due to the small box size, to proceed out of the matrix without depositing more energy. The atom struck is referred to as the primary knock-on atom (PKA) and all subsequently displaced atoms are called secondary knock-on atoms (SKAs). These SKAs, imparted with an energy $E_{\text{SKA}}$, will then move through the metal matrix and lose energy as they collide with other atoms and energy will be exchanged. The exchange of energy in the collisions is assumed to be elastic.

$$\begin{cases} E_{\text{SKA}} \geq E_d & \text{Dislodge new atom and make new SKA} \\ E_{\text{SKA}} < E_d & \text{Form interstitial dumbbell} \end{cases}$$

If the $E_{\text{SKA}}$ of the resting atom rises above the threshold displacement energy $E_d$, then the resting atom will be energized to vacate its lattice site on its own path and become another SKA in the cascade. When the energy of the SKA falls below the threshold energy and collides with a sitting atom, an interstitial dumbbell forms on that lattice site. Once formed, this dumbbell is open to recombination with the vacant sites left behind in the cascade. At the end of a cascade, a small number of vacancies and dumbbells that have not recombined are left in the simulation box.

Displacement cascades have been simulated using molecular dynamics (MD)\textsuperscript{16}, although it is cost prohibitive to computationally use for long term irradiation studies. Atoms do not stay on a rigid lattice in molecular dynamics simulations and the atoms are allowed to relax to more energetically favorable positions. This requires constant tracking of atomic locations and recalculation of the atomic interactions so that the timescale of MD simulations is in the nanosecond range. Relaxation of atoms is not accounted for in the KMC model with the atom strikes taking place instantaneously in a rigid lattice point. This sacrifice in precision allows the KMC model to achieve timescales that can reach irradiation doses up to 70 dpa and beyond. The irradiation mechanism also does not account for bonds between atoms with the $E_d$ of the atom only being dependent on the atomic species. A method validating the neutron irradiation
mechanism by tracking the number of displacements generated is provided in the Supporting Information as well as a description of the ‘dpa’ unit that measures irradiation damage.

6. Simulation Procedure

In order to study how irradiation damage impacts nano-oxides in 12YWT and 14YWT, the KMC simulations were first subjected to heat treatment at different temperatures and were then analyzed based on precipitate nucleation, growth, and composition. Any differences in the oxide characteristics between the two simulation conditions were noted. The final heat-treated systems are then subjected to neutron irradiation at varying doses and temperatures to observe nano-oxide changes for both low and high dpa. Additionally, KMC simulations were conducted on 14YWT at 633 K and 6.5 x 10^-7 dpa/s in order to compare with other experimental results and a brief exploration of longer-term irradiation was conducted.

III. Results

1. Precipitation Results under thermal aging

   A. Homogeneous and Heterogeneous Precipitation in the Presence of a Defect Sink

   We studied the influence of the grain boundary on precipitation and compare the results to those obtain in bulk materials carried in a previous study. The defect interaction with the grain boundary follows methods in previous work. The alloy of choice was similar to the commercial alloy 12YWT. The atomic concentrations for both model alloys of the key solutes Y, Ti, and O in the bcc Fe matrix are (0.13 at% Y, 0.4 at% Ti, 0.18 at%) for 12YWT and (0.08 at% Y, 0.27 at% Ti, 0.3 at%) for 14YWT. Other elements, such as Cr and W, were not included. Note that the atomic concentrations of the constituent solutes are not an exact reflection of the expected stoichiometry of the oxide nanoparticles. There are various reasons for this—research has shown that keeping the Ti:Y ratio above 1 and limiting excess oxygen in the metal matrix is important for the thermal stability of the oxides at high temperatures. These factors also limit the degree of coarsening in the system. Samples of another alloy, 14YWT, were heat treated in simulation alongside the 12YWT for later use in the irradiation simulations.

   A simulation box of the same size as the prior bulk precipitation simulations was constructed with a simulated grain boundary in the center. The grain boundary was represented by a perfect
planar sink perpendicular to the longitudinal direction where vacancies were annihilated once they migrated onto the boundary plane. Once the Fe-Ti-Y-O system was populated with the appropriate number of atoms and makes a supersaturated solution, the thermal precipitation simulation began. The simulations were run at 3 temperatures (1023 K, 1123 K, and 1223 K) for the 12YWT and at 1123 K for the 14YWT composition. The 1123 K simulation was compared to experimental results obtained by Alinger for the 12YWT$^7$ and Miller for the 14YWT$^6$. 

Figure 1 The evolution of oxide size with time with and without a grain boundary for the 12YWT composition at a) 1023K b) 1123K and c) 1223K.

Figure 1 compares the kinetic evolution at three temperatures for the 12YWT with and without a grain boundary in the box. The precipitation starts with rapid nucleation and growth of nano-oxides until most of the solute material is exhausted from the Fe matrix to reside in the oxides. A slow coarsening stage follows owing to the trapping of vacancies at oxide interfaces as shown in
Fig. 2. The higher vacancy concentrations are shown at the interfaces of the precipitates. This is expected as the precipitates act as defect sinks and trap the vacancies at the surface\textsuperscript{33}.

![Vacancy Heatmap](image)

**Figure 2:** Heatmap of vacancy locations in the 12YWT-1123K with a grain boundary during heat treatment

There was little difference in the average size of the oxides between simulations with and without a grain boundary. There was, however, a difference in the location of the oxides. While the oxides were evenly distributed in the bulk precipitation simulations in Figure 3a, the area around the planar sink in the grain boundary simulations was depleted of oxide precipitates as seen in Figure 3b. This precipitate free zone extends 1-2 nm away from the planar sink and is a common phenomenon in many alloy compositions\textsuperscript{34}. When considering the vacancy concentration near the grain boundary, there is a noticeable decrease due to the sink removing the defects. This reduction in vacancy concentration is a likely contribution to the lack of oxide formation in the region near the grain boundary as vacancies facilitate solute diffusion that leads to oxide as shown in Fig. 2.
B. Oxide Composition and Vacancy Concentration

The KMC model was further validated by comparing the composition of the oxides formed during the simulation against experimental findings. The oxide compositions in the KMC model were gathered at the end of the precipitation simulations. Tables 5 and 6 show the composition of the oxides formed in the precipitation heat treatments in systems with and without the grain boundary as well as their expected results from the literature. For both sets of simulations, the compositions of the oxides were very similar, suggesting that the defect sink had little influence on the composition of oxides outside its immediate vicinity. There was roughly a 1:1 ratio of metal to oxygen atoms (M:O) with more Ti atoms in the oxide than Y atoms. This is in relatively good agreement to the experimental results of the oxide composition, although the minor constituent Cr was absent from the oxide compositions since the element was excluded from the KMC model. The oxides deviated from the stoichiometry of the oxide chemical formula due to the unbalanced starting concentrations of solutes.

After thermal aging, the vast majority of the Y, Ti, and O atoms were associated with an oxide precipitate and the concentration of solutes in the Fe matrix corresponded to the solubility product
in iron. The cubical shape of the oxide precipitates shown in Fig. 3 tend to nucleate into matched expectations from Ribis.\textsuperscript{35}

| Material System                  | Y at% | Ti at% | O at% |
|----------------------------------|-------|--------|-------|
| 12-YWT KMC without GB           | 12.9% | 37.6%  | 47.9% |
| 12-YWT KMC with GB              | 12.7% | 36.1%  | 50.9% |
| 12-YWT Alinger with GB\textsuperscript{12} | 14.8% | 33.6%  | 39.4% |

Table 5 The atomic compositions of the Y-Ti-O oxides of the 12YWT -1123K heat treatment with and without a grain boundary in the simulation box and an experimental comparison.

| Material System                  | Y at% | Ti at% | O at% |
|----------------------------------|-------|--------|-------|
| 14YWT KMC without GB            | 12.1% | 36.9%  | 50.8% |
| 14YWT KMC with GB               | 12.0% | 36.4%  | 51.6% |
| 14YWT Miller with GB\textsuperscript{14} | 7.5 ± 4.3 | 42.2 ± 5.6 | 43.3 ± 5.3 |

Table 6 The atomic compositions of the Y-Ti-O oxides of the 14YWT -1123K heat treatment with and without a grain boundary.

2. Homogeneous and heterogeneous precipitation under irradiation

A. 12YWT Irradiation Simulations

The survivability of the oxides was simulated under irradiation environment. For this study, we used the end configuration from the 1123 K precipitation heat treatment. The oxide characteristics for the 12YWT-1123K simulation has a number density of $2.0 \times 10^{24}$ m$^{-3}$ with an average radius of 0.8 nm. The simulations were set up to mimic reactor environments in the same ranges as Wharry collected for their review\textsuperscript{11}. These irradiation simulations explored the influence of temperature and dose rate on oxide characteristics by varying the irradiating conditions for each set of samples. The dose rate, based on average displacements per neutron strike, had a range of three possible values: $10^{-3}$ dpa/s to determine resistance of the oxides to dissolution under very heavy irradiation, $10^{-5}$ dpa/s to determine the results at a dose rate closer to experimental rates, and $10^{-4}$ dpa/s to observe any patterns from the direction of dose rate. Three irradiation temperatures were evaluated to observe the temperature dependence of oxide survivability. The temperatures were 673 K, 773 K, and 873 K so as to capture the widest range of reactor conditions.

Figure 5 shows the average radius of the oxides over accumulated damage dpa for all tested temperature and dose rate combinations. Across all irradiation regimes, a small decline was seen in the size of the oxides that sharply began at the 1-4 dpa region before appearing to reach a plateau in the 4-8 dpa range. The oxides experienced less atom loss with decreasing temperature. At the lowest dose rate ($10^{-5}$ dpa/s), there was a higher reduction in oxide size compared to the oxides irradiated at the same temperature but at higher dose rates. However, differences in the precipitate
size per dose rate declined with decreasing temperature with the 673 K batch showing little variability between dose rate results.

![Average Radius (nm) vs. dpa of Y-Ti-O nano-oxides](image)

**Figure 5** Evolution of the average oxide size in 12YWT over total accumulated dose at a variety of irradiation regimes

![Number Density](image)

**Figure 6** Evolution of the number density of oxides in 12YWT over total accumulated dose at a variety of irradiation regimes

Figure 6 shows the change in the number density of oxides in 12YWT over accumulated dose dpa for all tested temperature and dose rate combinations. Similarly, to the average size findings,
there was a sharp initial drop in the number density before reaching an apparent plateau in the 4-8 dpa range. This drop in oxide number density is observed in other neutron irradiated samples of NFAs\textsuperscript{13}. More oxides were dissolved at higher temperatures. This was most pronounced at the 873 K temperature while there was only at most a 10% decline in the number density at the 673 K and 773 K temperatures. There was more oxide dissolution at low dose rates than at higher dose rates across all temperatures tested, with the 873 K $10^{-5}$ dpa/s case experiencing the largest decline with nearly a 30% loss in number density.

![Graph](image1.png)

Figure 7 Average radius and number density of the nano-oxides in 12YWT-1123 K of a particular dose versus irradiation temperature.

Figure 7 visualizes the influence of temperature and dose rate on the average size and number density of the oxides at 8 dpa. As expected, the average radius declines with irradiation temperature; however, an interesting finding was nano-oxides showing more stability at higher
rather than lower dose rates. This is likely due to the increased point defect population at higher dose rates in which the vacancies bring back solute material at a faster rate to the oxide. The decline in average size at 873 K can also be attributed to vacancies as the higher temperature keeps the vacancy population down so the oxides are not replenished with solutes at a sustainable rate than at 673 K and 773 K. Ribis’s investigations with ion irradiation of ODS steels found the vacancy concentrations are critical to the stability of nano-oxides and its dependence on temperature can explain the difference in nano-oxide irradiation stability at different temperatures\textsuperscript{36}.

Precipitate Shape

The shape of the precipitates was visually inspected under thermal aging and neutron irradiation. Any deviation from the expected cubic shape with sharp interfaces was noted. For thermally aging simulations, a large perfectly cubic Y-Ti-O oxide is aged in simulation until an equilibrium shape emerges. Figure 8 exhibits a representation of precipitate thermally aged at all three irradiation temperatures. The theoretical equilibrium shape for the oxide is displayed in Figure 8d and is created according to the interface energies in Table 7 using the Wulffmaker\textsuperscript{37} program. Both simulation and theory match well and both reproduce the experimental shape observed by Ribis\textsuperscript{35}.

| Interface Energy | Y-Ti-O (BBM) |
|------------------|--------------|
| $E_{100}^\gamma$ | 0.41         |
| $E_{110}^\gamma$ | 0.52         |
| $E_{111}^\gamma$ | 0.63         |

Table 7: Interface energies from the broken bond method (BBM).
Figure 8 Equilibrium shape of the Y-Ti-O oxide at a) 673 K b) 773 K c) 873 K. Precipitates are compared with expected equilibrium shape d) of the nano-oxides made using Wulffmaker\textsuperscript{37}. Purple = <100>, Blue = <110>, Yellow=111>.

The equilibrium shape simulations performed in a prior study were repeated at the same temperatures in the irradiation simulations (673 K, 773 K, 873 K). The resulting equilibrium shapes are displayed in Figure 8. The oxide precipitates were dominated by the <100> interface with smaller areas of the <110> and <111> interfaces. The oxides in the irradiation simulations continued to maintain this shape as shown in Figure 9.

Figure 9: 12YWT-1123 K after irradiation at 773 K at a dose rate of $10^{-3}$ dpa/s to a total dose of 8 dpa. Green spheres: Ti atoms, Grey spheres: Y atoms, Red spheres: O atoms.

Figure 9 is an image of an oxide in 12YWT-1123 K after irradiation 773 K at a dose rate of $10^{-3}$ dpa/s to a total dose of 8 dpa and was representative of the changes in oxide shape seen in all
the simulations. With increasing irradiation, these faces became more diffuse and irregular while maintaining a cubic/rectangular shape, which was also in line with expectations\textsuperscript{38}.

B. 14YWT Irradiation Replication Simulations

After completion of the irradiation simulations of the 12YWT-1123 K samples at the three test temperatures and three dose rates, the general response of the oxides to irradiation in 14YWT-1123 K proceeded.

Figures 10 and 11 show the average radius and number density change with accumulated damage in 6 simulations of 14YWT at the conditions described in Aydogan\textsuperscript{39}. There was a decrease in the average radius that appeared linear with the accumulated dpa damage. Reduction in nano-oxide size under irradiation at these temperatures has been shown in many other experimental studies\textsuperscript{40}. A plateau did not appear to have been reached like the 12YWT irradiation simulations. The number density of the oxides remained constant during irradiation across all samples.

![Average Radius over dpa for the 14YWT-1123K irradiation at 633K. Red dot represents Aydogan’s observations.](image)

**Figure 10** Average radius over dpa for the 14YWT-1123K irradiation at 633K. Red dot represents Aydogan’s observations.\textsuperscript{39}.
Figure 11 Change in the number density over dpa for the 14YWT-1123 K irradiation at 633K. Red dot represents Aydogan’s observations.

Figure 12 Oxide size distributions of 14YWT before and after irradiation

Figure 12 shows the size distribution of the oxides across all 6 simulations before and after irradiation to 7 dpa. None of the oxides were shown to have fully dissolved, which is in line with expectations from the number density results. However, all of the oxides experienced a decrease in their size with no irradiation induced growth shown. This concurs with the average size and number density trends seen in Figures 10 and 11.

- Composition Change after Irradiation

The nature of neutron irradiation leads to shifts in the composition of the oxides in the NFA, which could affect their performance and stability. The composition change in the oxide precipitates at the end of the irradiation treatment were compared against the values at the
beginning of the simulation for the 12YWT and 14YWT compositions. Tables 8 and 9 show the composition of the oxides after irradiation and their respective compositions prior to irradiation. In both cases, the proportion of oxygen in the oxide goes up as well as the amount of Fe in the oxide. In turn, the proportion of Y and Ti in the oxides decreases. The decrease in Y concentration following increasing temperature matches well with other irradiation damage experiment. There is no consistent variation in oxide composition with dose rate, with the composition being more strongly dependent on temperature. The proportion of Ti in the oxide declined the most over the course of the irradiation, particularly as the irradiation temperature increased. Nearly a third of Ti atoms in the oxide were expelled at 873 K. This high reduction in Ti concentration by neutron irradiation is observed in other experimental results. One of the reasons is the higher diffusion coefficient of Ti compared to Y or Fe.

| Composition | O at%  | Y at%  | Ti at%  | Fe at% |
|-------------|--------|--------|---------|--------|
| 14YWT from KMC at 0 dpa | 51%    | 12.0%  | 36%     | -      |
| 14YWT KMC After Irradiation | 54.1%  | 9.8%   | 28.85%  | 7.14%  |
| 14YWT Miller | 43.3 ± 5.3 | 7.5 ± 4.3 | 42.2 ± 5.6 | - |

**Table 8 Composition of oxides after irradiation to 7 dpa at 6.5 × 10⁻⁷ dpa/s**

| Dose Rate (dpa/s) | O at% | Y at% | Ti at% | Fe at% |
|-------------------|-------|-------|--------|--------|
| 12YWT Before      | N/A   | 50.94 | 12.76  | 36.17  |
| 673 K             | 10⁻³  | 56.10 | 10.23  | 28.18  |
| 673 K             | 10⁻⁴  | 55.57 | 10.45  | 28.48  |
| 673 K             | 10⁻⁵  | 55.58 | 10.14  | 27.77  |
| 773 K             | 10⁻³  | 58.61 | 9.71   | 26.08  |
| 773 K             | 10⁻⁴  | 58.6  | 9.51   | 26.34  |
| 773 K             | 10⁻⁵  | 58.789| 9.53   | 25.63  |
| 873 K             | 10⁻³  | 61.58 | 9.14   | 22.45  |
| 873 K             | 10⁻⁴  | 62.44 | 8.88   | 22.27  |
| 873 K             | 10⁻⁵  | 62.35 | 9.00   | 22.38  |

**Table 9 Composition of oxides in 12YWT after irradiation to 8 dpa per irradiation regime.**

- Composition Evolution
The composition of solute atoms in the oxides was tracked over received dose. The evolution of the oxide composition was plotted and analyzed for notable trends. Figure 13 shows the composition evolution during the irradiation simulations. As the total accumulated dose increased, more of the Y and Ti solutes were ejected from the oxides into the bulk. Fe was gradually introduced as a replacement component in the oxide, going from near non-existent to up to 7 at%.

All cases appeared to be heading towards a plateau near the end of the simulation, suggesting that the oxide composition would reach an equilibrium value where solutes are replaced as quickly as they are ejected from the precipitates. Again, through this visualization, the composition was more strongly influenced by the irradiation temperature than the dose rate.

Figure 13 Evolution of oxide composition in 12YWT over accumulated dose at various temperatures and dose rates. Red=Oxygen, Green=Titanium, Blue=Yttrium and Purple = Iron
Figure 14: Average vacancy concentration heat map of the 14YWT under neutron irradiation at 773K and $10^{-3}$ dpa/s.

Figure 14 shows the vacancy heat map of the 14YWT under irradiation. Like with precipitation simulations under thermal aging, the vacancy spends a lot of time at the oxide interfaces than in the bulk. This is due to the attractive interactions between the oxide constituent atoms and the vacancy compared to Fe. An earlier investigation found a binding energy between the vacancy and the oxide around 1.1 eV$^{22}$. Additionally, even under high irradiation, there is still a lower vacancy concentration in the grain boundary region than in the outer regions due to the grain boundary’s role as a defect sink.

C. Higher Dpa Regime

Since the NFAs are expected to receive a lifetime dose in the 100 dpa range, an investigation of the stability of the nano-oxides under longer term irradiation was examined. It is presently impractical to extend the simulated irradiation regimes past 8 dpa for all conditions. The single
regime selected for long-term irradiation was chosen primarily for the real-time speed of completion as opposed to the other regimes. In this case, the irradiation regime at 873 K and $10^{-3}$ dpa/s was used to take three 12YWT samples to a total dose of 66 dpa. Like Section II.5.B, the evolution of the oxide characteristics as a function of dose was recorded for analysis.

After observing an apparent plateau in the decline of the size and number of oxides in the system across all irradiation regimes, an additional limited investigation was conducted to see if that plateau represented the emergence of a steady-state or only a temporary metastable stage. Three samples from a single irradiation regime (873 K at $10^{-3}$ dpa/s) were taken further to 66 dpa and the evolution of oxide characteristics over dpa was recorded.

![Figure 15](image1.png)

**Figure 15** The evolution of 12YWT oxide characteristics in long-term irradiation simulation at a single irradiation regime (873K at $10^{-3}$ dpa/s)

Figure 15 shows the evolution in oxide size and number density as they were irradiated to a total dose of 66 dpa at 873K at $10^{-3}$ dpa/s. After 8 dpa, the plateau in oxide size started to decline again before reversing and increasing in size after 12 dpa. The change in the number density of oxides continued to hold its initial downward trend through the whole simulation and no longer mirrored the change in oxide size. The evolution reached an apparent steady-state after 54 dpa. These results follow experimental results of neutron irradiation damage at high dpa regimes with an increased average radius and decrease in number density\textsuperscript{12}. 
Figure 16 Oxide distributions of the 12YWT-1123K a) before neutron irradiation, b) after neutron irradiation with a total dose of 66 dpa at 873K at a dose rate of $10^{-3}$ dpa/s

Figure 16 shows pictures of the 12YWT simulation box before and after neutron irradiation to 66 dpa. In the irradiated sample, there was a higher density of free solutes Ti and Y in the Fe matrix, separated from their original oxides from irradiation. Many of the original oxides dissolved under irradiation, with oxides around the grain boundary suffering the most losses. The grain boundary itself was largely devoid of free solutes and no new oxide precipitates were found at the grain boundary.

The tendency of a solute species to enrich or deplete at defect sinks is attributed to the inverse Kirkendall effect where preferential transport of the solute via the vacancy or dumbbell migration compared to matrix atomic species leads to segregation around defect sinks. Was$^{42}$ developed a formulation that predicts whether a solute enriches or depletes at defect sinks using the diffusivities of the solute and matrix atoms.
\[
\frac{d_{AV}}{d_{BV}} - \frac{d_{AI}}{d_{BI}} \rightarrow \begin{cases} < 0 & \text{Enrichs} \\ > 0 & \text{Depletes} \end{cases}
\] (6)

The diffusivities \(d_{XV}\) and \(d_{XI}\) of atomic species X are via vacancy and dumbbell migration respectively. To check the direction of segregation using Eq. 6, atomic species A is the solute (Y or Ti) and atomic species B is the matrix atom (Fe).

| \(\frac{d_{AV}}{d_{BV}} - \frac{d_{AI}}{d_{BI}}\) | A=Y B=Fe | A=Ti B=Fe |
|-----------------|---------|---------|
| 673K            | -10.32  | 19.68   |
| 773K            | -7.84   | 31.60   |
| 873K            | -6.23   | 43.33   |

Table 2: The Ratio of Diffusivity of Y and Ti with Fe

Table 10 shows the diffusivity ratios for the Y and Ti solutes in bcc Fe at all irradiation temperatures. There was a slight preference for enrichment for the Y atoms at defect sinks while the Ti atom was more strongly led to depletion. The presence of oxides and the supersaturation of the Y and Ti solutes in the Fe matrix was the likely cause of the differences in predicted behavior for Y segregation, as Was’s formulation assumes these conditions are not present.

The nano-oxides are suspected to suppress the point defect population and therefore slow down the diffusion processes that drive segregation. To investigate this, the KMC simulations were run at three temperatures (673 K, 773 K, and 873 K) at a single does rate \(10^{-3}\) dpa/s for two starting configurations with the first being a simulation box of pure Fe with no other solutes and the second being the 14YWT configuration. The average concentration of point defects in the bulk matrix (not bounded to the oxides) is recorded and compared between the two cases.
Figure 17: The concentration of point defects in pure Fe and 14YWT vs temperature. a) Vacancy Concentration. b) Dumbbell Concentration.

Figure 17a and 17b shows the average concentration of vacancies and dumbbells respectively in the simulation box during irradiation at $10^{-3}$ dpa/s over temperature. The plots show the nano-oxides in 14YWT do have a suppressing effect on the average population of point defects. This suppression effect weakens with increasing temperature. At 873 K, there is almost no difference in the concentration of vacancies. This is likely due to the high temperature speeding recombination and diffusion to the grain boundary so much that the vacancy concentration does not rise much above thermal equilibrium.

IV. Discussion

1. Precipitation
The precipitation simulations showed a pattern of increasing oxide size with increasing temperature, which was anticipated due to the thermodynamics of precipitation. As the temperature rose, the solubility product of the oxide also increased, making the critical radius of a stable dispersoid nuclei larger and less frequently achieved. The free solutes mass of the fewer stable nuclei resulted in a lower number density of oxides that were larger in size. The size, number density, and composition of the oxides in both 12YWT and 14YWT compared favorably to experimental results. The absence of solutes such as Cr in the KMC could be a factor in any discrepancies. The shape of the precipitates was also observed with the oxides in the precipitation heat treatments taking a cubic shape, with broad <100> interfaces and small areas of <110> and <111> interfaces at higher temperatures, which was expected from our observations. Equilibrium shape simulations that were later performed affirmed that the cubic shape represented the equilibrium shape when the KMC forced a preexisting oxide to reshape into the equilibrium shape seen in experiments.

The influence of the grain boundary on precipitation was studied at the same temperatures as bulk simulations in a prior study. The results found little difference in the average radius and number density of the oxides between the bulk and grain boundary simulations. There were differences in oxide distribution between the two cases as no oxide precipitates formed in the immediate vicinity of the planar sink, leaving a noticeable gap. There is literature that observed the formation of oxides at the grain boundary. These grain boundary nano-oxides were typically larger than the oxides in the intergranular region. It has been theorized that the presence of interstitial elements such as C and N play a role in facilitating the formation of nano-oxides at the grain boundary, so the absence of these elements could explain the absence of grain boundary nano-oxides.

Another factor to consider is the opportunity for vacancy movement at the grain boundary. Since the sink annihilated the point defects on contact, this region had a much lower average concentration of vacancies than regions away from the boundary. Thus, there was less opportunity for atomic diffusion around the grain boundary, which inhibited the nucleation of the Y-Ti-O precipitates. Given NFA’s known inclination towards rapid oxide nucleation, the matrix would likely be depleted of free solute material before any nucleation near the grain boundary could occur. Additionally, segregation of intergranular Ti, Y, and O atoms to the grain boundary during
thermal heat treatments was not found by Alinger\textsuperscript{5}, leaving less available material to form grain boundary nano-oxides.

2. Irradiation

   A. Overall Survivability

   The neutron irradiation simulations found that the oxides behaved in an expected manner in response to irradiation. They appeared resistant to dissolution even at the relatively high dpa rate of $10^{-3}$ dpa/s with the high dose rate appearing less effective at dissolving oxides. The presence of vacancies worked to heal the oxide structures even when the displacement cascade ejected solutes from the oxides. Nevertheless, there was still a decrease in the overall size of the oxides over the irradiation regime. Through observations of the size distributions before and after the irradiation, it was seen that the smallest oxides quickly dissolved while the larger oxides were more stable. There were no oxides larger than 1 nm in radius for the 12YWT cases at accumulated damage $>4$ dpa. The oxide stability could also be a product of the inherent KMC set-up. Chen found that oxides coherent with the Fe matrix were more stable than incoherent oxides\textsuperscript{43}, meaning that the oxides in the rigid lattice KMC set-up may have too much stability.

   Inherent stability is likely explained by Nelson-Hudson-Mazey’s theory of stability, which is dependent on two competing forces, both caused by irradiation\textsuperscript{44} where irradiation that expels debris from oxides is the cause of oxide loss and radiation enhanced diffusion drives the regrowth of the oxides. Since vacancies drive nucleation and growth during the heat treatment phases, the increased vacancy concentration due to irradiation has a ‘healing’ effect on the damaged oxides and drives restoration of the oxides. So we see more atomic loss in oxides when the vacancy population is kept to a relative minimum at 873K. Smaller oxides proportionally lost more material in the irradiation cascade and were, therefore, more susceptible to dissolution.

   The long-term irradiation simulations at 873K and $10^{-3}$ dpa/s saw the decline in oxide size reverse itself and had the surviving oxides grow larger than the original average. Atomic material for this growth comes from oxides dissolved during irradiation, resulting in a decrease in the oxide number density. This radiation induced coarsening of the oxides is seen in similar NFAs\textsuperscript{12}.

   A compositional analysis of the oxides after irradiation for both 12YWT and 14YWT found an overall decrease in the proportion of Ti atoms in the oxide with a corresponding increase in the
Fe atoms in the oxide. The Ti atoms accounted for most of the solute atoms in the matrix. Since the Y atoms bound more strongly to oxygen than Ti, the Y atoms were less likely to separate from the oxide and were more likely to rejoin the oxide after being ejected. Overall, across the temperatures sampled, the oxide compositions generally approached a stable plateau after irradiation to 8 dpa.

B. Precipitate Shape

During the heat treatments, the oxides precipitated into cubical shapes that were in line with expectations, giving another measure of validity to the KMC model. The shape of a precipitate was determined by the differences in energies at the oxide/matrix interfaces at various orientations. If the energetics of the system are set up properly, then the oxides formed will match experimental observations, which was found to be the case across all simulations. The shape was orderly with sharp interfaces that became more diffuse upon irradiation, owing to the constant dislodging of atoms by irradiation. These interfaces would likely become orderly again when the irradiation ceased and the oxides interacted with the thermally produced vacancies again.

C. Effect of the Dose Rate

When examining the relationship of dose rate with survivability of the oxides, the following relationship was revealed: with the higher dose rate leading to larger loss of size among the oxides and at the lowest dose rate, there was less of a decrease in oxide size, although at both of the lowest dose rates, $10^{-4}$ and $10^{-5}$ dpa/s, the difference in oxide size was very small. The lower dose rates equated to a smaller supersaturation of point defects, which slowed the diffusion that heals the oxides and causes them to experience more atomic loss by the 8 dpa range. All of the irradiation simulations with the 12YWT reached a certain plateau where the average size, number density, and composition did not change as quickly as before. This is where enough solutes have been ejected into the matrix to provide a sufficient source of solutes for vacancy diffusion to start to stymy oxide material loss.

The limited long-term irradiation investigation, conducted to further explore the extent of oxide stability, found that this period of stability after 8 dpa was temporary and oxide loss continued. Eventually, a period was reached where the oxide loss stabilized after 54 dpa. The average size and number density of the oxides remained roughly constant until the end of the simulation at 66
dpa. This was where the smallest oxides dissolved completely and the more stable larger oxides remained and where the loss and gain of atomic material in the oxides cancel each other out.

D. Segregation

In the irradiation simulations, there was a lack of segregation to the grain boundaries of the solute Y, Ti, and O atoms. There even appeared to be an inverse Kirkendall effect where the solutes were depleted in the region around the grain boundary. The lack of segregation of Y-Ti-O elements has been observed in experimental observations of irradiated NFAs with an apparent preference for the solutes to return to the oxides\textsuperscript{45}. Other studies have seen both segregation of Ti\textsuperscript{46} and no segregation\textsuperscript{47} to the grain boundary reported in some cases; however, these experiments involved heavy ion irradiations. The simplistic description of the grain boundary in the KMC could have influenced the resulting segregation profiles. Field\textsuperscript{48} showed that Cr segregation could be highly dependent on grain boundary structure. The oxides also suppress the point defect populations, thus partly stifling the degree of segregation.

E. Nano-oxide solute ejection and diffusion

Using the diffusivities of the solutes, Eq 6 predicted that Ti depletes and Y enriches at defect sinks from Was’s formulation. While the tendency of Y to deplete is in contrast to the predicted Y behavior at defect sinks, factors unaccounted for in the formulation, such as the influence of oxides, should also be considered. During irradiation, atoms are ejected from the oxides into the Fe matrix. Once in the matrix, there are several destinations for the atoms: 1) return to the original oxide, 2) join a preexisting oxide, 3) form a new nucleate with other ejected solutes, and 4) congregate at the grain boundary and possibly precipitate a new phase. The oxides acted as competing sites for Y segregation, which dampened the level of enrichment that could be achieved at the grain boundary. The Y atoms expelled from the oxides, having only been knocked a short distance, were inclined to rejoin the oxide by both the supersaturation of Y in Fe and the preferential transport of Y to the oxides. The disproportionate amount of Ti atom loss in the oxides compared to Y atoms lends further evidence of a Kirkendall effect where Y atoms enrich at the oxides while Ti is driven to deplete into the oxide region. Point defects still transported the Ti atoms to the oxides but at slower rates than Fe and Y, resulting in composition loss in the oxide.
In visual observations of the oxide, there was no oxide precipitation in the region around the grain boundary and few stable precipitates elsewhere. Instead, the free solutes rejoined the pre-existing oxides to heal the damage from irradiation. While there was a greater concentration of free solutes in the Fe matrix, there was little increased concentration of solutes in the region around the simulated grain boundary. The oxides closer to the grain boundary were even more susceptible to the dissolution. This behavior is in agreement with the theory that the defect populations help stabilize oxides since the region around the defect sink has a lower average point defect concentration than the rest of the system. So, the oxides in the grain boundary region are not healed as quickly and, therefore, suffer dissolution under irradiation. Binding of the vacancies to the oxide interfaces can also play a role in segregation behavior as it has been noted that similar vacancy binding limits the migration of point defects and makes them more susceptible to recombination instead of journeying to the sink (and taking solutes with them) for annihilation. There would, therefore, be less segregation at the grain boundaries.

F. Replication of the 14YWT neutron experiment.

The oxide response to irradiation in the 14YWT replication simulations showed good agreement with the results from Aydogan\(^{39}\). There was a marginal decrease in the average size of the oxides and none of the oxides dissolved in the face of irradiation damage, although there were occasional short-lived oxides formed from the irradiation debris that quickly dissolved under irradiation. These results display the inherent survivability of oxides in the environments required in nuclear reactors.

With the KMC model showing agreement with experimental observations during heat treatment and irradiation, it can be used for larger research projects, possibly with an artificial intelligence component. The model can be further extended to observe more phenomena that take place under irradiation. The next steps for this model are to include insertion of transmutation He into the system. Then observations can be made of the nucleation of He bubbles into the NFAs and the degree to which the nano-oxides inhibit the formation of bubbles at the grain boundaries.

V. Conclusion

A Kinetic Monte Carlo model was created and parameterized for the Fe-Ti-Y-O system. Several simulations of the nucleation and growth stages of nano-oxide \(Y_2Ti_2O_7\) formation along
the grain boundary were observed for temperatures of 1023 K, 1123 K, and 1223 K for the 12YWT alloy. The characteristics of the oxides formed were in good agreement with experimental results in size, number density, and shape for the bulk precipitation. The influence of the grain boundary on oxide characteristics were found to be limited in this system. Later, the model subjected the same oxides to neutron irradiation and the changes in oxide size were recorded. The results found that the oxides were stable against irradiation but suffered a gradual decline in size as the material became more damaged. This was true at all temperatures and dose rates studied. An attempt was made to replicate findings for a neutron irradiation experiment of 14YWT and found good agreement with the findings showing little change in oxide characteristics.

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Conflicts of Interest

The authors declare no conflicts of interest with the present work.

Supporting Information:

Neutron Irradiation Mechanism

With the adoption of the ‘dpa’ unit in the literature, neutron absorption cross-sections and neutron fluxes are not required. It has become common for the rate of accumulated damage from irradiation to be expressed as the simple dpa/s. While the damage rate in any material will vary by depth, for small targets like the simulation box, the dpa/s remain practically constant across the entire volume. The probability of a neutron strike $\Gamma_{\text{neutStrike}}$ is set to the user-inputed dose rate $G_{\text{dpa}}$ in dpa/s and adjusted using the ratio of number lattice points in the box $N_{\text{box}}$ and the average number of displacements in a cascade $\overline{N_d}$. This ensures that the correct number of neutron strikes occurs to give the right dpa over the right time period.

$$\Gamma_{\text{neutStrike}} = G_{\text{dpa}} \times \frac{N_{\text{box}}}{\overline{N_d}}$$  \hspace{1cm} (S1)

The $\overline{N_d}$ from the resulting cascade is estimated by the following equation:
\[ \bar{N}_d = \frac{AE_n}{4 + E_d} \quad \text{(S2)} \]

\[ \Lambda = \frac{4A}{(1+A)^2} \quad \text{(S3)} \]

\( E_n \) is the initial energy of the neutron, \( A \) is the atomic mass number, and \( E_d \) is the threshold displacement energy. For Fe, the \( E_d \) is set to 40 eV based on literature values. Inside the oxides, the threshold displacement energy for the atoms is set to 57 eV, which is tied to other irradiation studies\(^{50}\). Note that these formulas represent an average rather than a set constant\(^{51}\). This is a general relationship from Kinchin and Pease\(^{52}\) that has been found to overestimate the number of displacements from neutron irradiation. Thus, the neutron irradiation is validated by tracking the number of displacements generated by a single displacement cascade and averaging over several trials. For a single 1 MeV neutron striking an all Fe matrix, the resulting displacement cascade should be around 430 displacements if Eq. S2 and Eq. S3 are followed. A validation procedure was developed and utilized below.

Validation Procedure:

1. Construct a simulation box 100X100X100 of pure Fe with no defects.
2. Track 3000 separate displacement cascades caused by 1MeV neutrons in the box.
3. Find the average \( \bar{N}_d \) of displacements per cascade in the KMC and compare against prediction.
Figure S1 is a histogram of the collected number of displacements in each of the 3000 neutron strikes. The average $\overline{N_d}$ was found to be 430.9 displacements per neutron strike in the pure Fe, which aligns with the prediction from the formulas. From this accounting of $\overline{N_d}$, the displacement cascade mechanism is proven to be usable for the KMC.

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