

Phase Stability in Nuclear Structural Steels

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To my family, for their tireless love and support.

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*The heights by great men reached and kept
Were not attained by sudden flight,
But they, while their companions slept,
Were toiling upward in the night.*

*Standing on what too long we bore
With shoulders bent and downcast eyes,
We may discern — unseen before —
A path to higher destinies,*

*Nor deem the irrevocable Past
As wholly wasted, wholly vain,
If, rising on its wrecks, at last
To something nobler we attain.*

— Henry Wadsworth Longfellow

Abstract

The operating conditions for fusion reactors are expected to be significantly harsher than existing fission light water reactors. As a result, structural steels need to be developed to meet the demands of higher temperatures, doses, and more energetic neutron damage. Control of secondary phases in a material's microstructure is instrumental towards maintaining acceptable mechanical properties and radiation tolerance. Here we focus on phase stability under irradiation in austenitic stainless steel (AuSS), which is commonly used for LWR core internals and oxide dispersion strengthened (ODS) ferritic alloys, which are actively being developed for fusion reactor applications. First, we discuss which factors affect the ballistic dissolution susceptibility of different solute nanocluster species by comparing the reponse of Cu- and Ni-Si-Mn-enriched solute nanoclusters in a 304L AuSS to neutron and ion irradiations. It is revealed using the Heinig precipitate stability model that the initial solute concentration gradient adjacent to a cluster's interface affects the thermodynamic driving force for radiation enhanced diffusion solute recovery. Next, we investigate over the fusion-relevant temperature range how phase instabilities contribute to hardening and embrittlement in ODS alloys. Mechanical testing of the ODS alloys after neutron irradiation demonstrates irradiation hardening even at temperatures where reduced activation ferritic/martensitic steels typically recover. There was no evidence of hardening suppression from the high initial sink strength of the alloys. With an eight feature hardening model, we reveal that Cr-enriched

nanoclusters are the primary contributor to the observed hardening under irradiation in high-Cr ODS alloys. Lastly, we consider how high dose neutron exposure affects the phase stability of oxide nanodispersoids. Using transmission electron microscopy, we reveal that at sufficiently high doses (~ 50 dpa), crystalline oxides are amorphized while Fe and Cr from the matrix enters the particles by ballistic injection and is able to agglomerate and recrystallize forming crystalline islands. These observations challenge the traditional assumption that oxide nanodispersoids are stable under irradiation.

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Chapter 1

Introduction

From decades of experience with fission light water reactors (LWRs), it is clear that structural materials play a critical role in a nuclear reactor's safety, energetic efficiency, and sustainability. In general, plant operating conditions are limited by material degradation issues. Radiation induced hardening and embrittlement, phase instabilities from radiation-induced precipitation, volumetric swelling due to cavities, radiation creep, and high temperature helium embrittlement have all plagued LWR core structural components [3]. The prevalent mode of radiation damage depend upon irradiation temperature, defect generation rates, and total defect concentrations (measured in displacements per atom and abbreviated as dpa). Current LWR structural materials, which are mainly austenitic stainless steel (AuSS) variants, are likely to be inadequate for the higher operating temperatures and displacement damage levels of Generation IV and fusion reactors under development. Figure 1.1 illustrates the dose and temperature operating conditions envisioned for each design concept. The structural materials selected for these designs will introduce important limitations to operating goals, which will in turn affect the safety, thermal efficiency, and cost efficiency of plants.

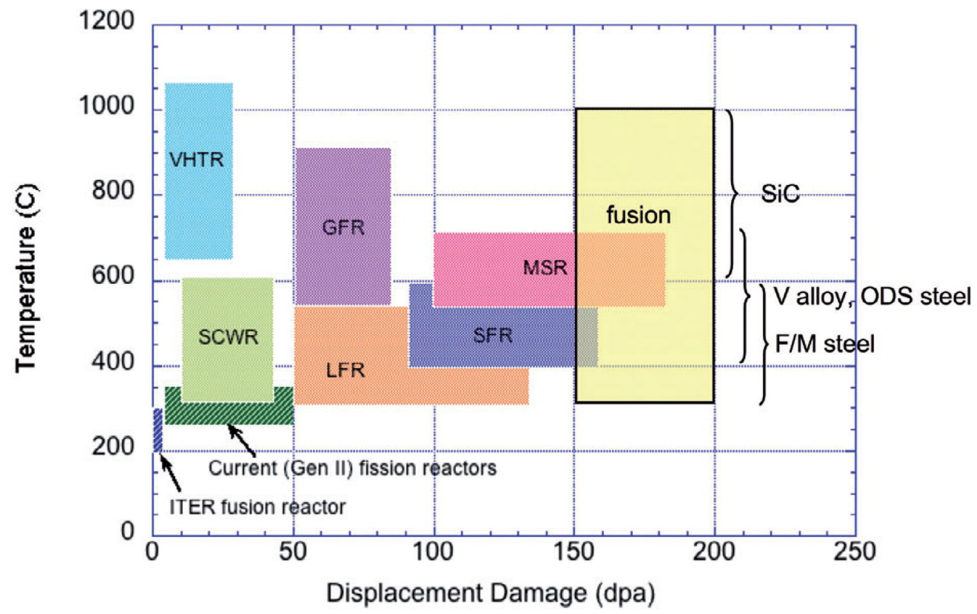


Figure 1.1: A schematic showing the expected dose and temperature operating conditions for various reactor designs. The Very High Temperature Reactor (VHTR), Super Critical Water Reactor (SCWR), Lead Fast Reactor (LFR), Gas Fast Reactor (GFR), Sodium Fast Reactor (SFR), and Molten Salt Reactor (MSR) are all Generation IV fission reactor concepts. Reprinted from [3].

The first wall/blanket is a vital structure in fusion reactor designs, which will influence power extraction, radiation shielding, and tritium breeding. Candidate materials for the first wall/blanket structure must possess excellent thermal conductivity, low thermal expansion, sufficient cavity swelling resistance, and acceptable mechanical properties [21, 22, 23]. In addition, chemical compatibility with selected coolants and tritium breeding materials is necessary. For ITER being built in France, the blanket structures will be made from austenitic stainless steels (AuSS). Austenitic were selected because they are already used extensively in the nuclear industry and are therefore fully code qualified. However, austenitic stainless steels are far from the ideal structural material as they suffer from low surface heat capacity, high nuclear activation, and low cavity swelling resistance above about 350 °C [24].

The European demonstration (DEMO) reactor, which will see materials exposed to higher damage levels, will alternatively have first wall and blanket structures composed of reduced activation ferritic martensitic (RAFM) steels. RAFM steels are similar to ferritic martensitic steels used commercially for petrochemical and conventional power plants, such as Grade 91 (9Cr-1Mo wt.%), however, Mo is replaced with W and/or V for strength (especially at high temperatures), hardness, and toughness, while Nb is replaced with Ta to promote carbide formation [25]. The removal of Mo and Nb is desired to reduce the concentration of long-lived solid transmutation products.

While RAFM steels offer an improvement over AuSS, it still appears that these alloys will be limited to $\sim 20 - 50$ dpa based on void swelling in the range of 400 – 500 °C [6]. Besides potential dose limitations, the temperature range for safe reactor operation with RAFM steels is somewhat limited. Radiation-induced low temperature hardening and embrittlement (LTHE) below 400 °C degrades fracture toughness [19, 26, 7]. In addition, the projected upper operating temperature for

RAFM steels is limited to 550 – 600 °C due to poor creep strength and thermal aging properties [6, 7].

To expand the operating temperature window for fusion reactors, oxide dispersion strengthened (ODS) steels are being developed as the next generation of nuclear structural materials. In particular, the superior creep properties of ODS steels make them suitable for operating temperatures as high as 650 °C for martensitic ODS and 750 – 800 °C for ferritic ($> 11\%Cr$) ODS [6]. However, there is a lot of information on the irradiated properties of ODS alloys that is still needed, particularly regarding LTHE.

Whether the structural steel of interest is a commonplace AuSS for LWR core internals or a novel ODS alloy being explored for fusion applications, phase stability under irradiation is a central concern since solute nanoclusters, precipitates, and dispersoids each can play a crucial role towards a material’s radiation resistance and mechanical performance. For example, a high density of fine dispersoids may help reduce the concentration of point defects produced during irradiation or trap harmful transmutation gases [27, 28, 29, 30]. On the other hand, significant precipitation under irradiation can cause undesirable hardening and embrittlement or deplete the matrix of important alloying elements [6, 31]. Thus, a fundamental understanding of phase behavior under irradiation is valuable for predicting the performance of materials for various reactor designs.

The term phase stability is quite broad and can be used in reference to either sink strength, crystallographic structure, or chemistry. Figure 1.2 schematically depicts the various processes that contribute to phase stability. The sink strength of a phase is calculated based on size and number density, and therefore may be altered by processes such as radiation enhanced precipitation (REP), radiation induced precipitation (RIP), ballistic dissolution, inverse Ostwald ripening, or radiation enhanced Ostwald ripening. On the other hand, disordering or amorphization may

impact the crystallographic structure. Finally, the chemistry of a phase may be affected by radiation modified precipitation, radiation induced segregation (RIS), or ballistic mixing. Many of these processes are discussed in greater detail in Chapter 2.

Other relevant concepts from radiation damage theory are also introduced in Chapter 2, and literature on AuSS and ODS steels is discussed. Damage rate, temperature, and dose are the primary variables that affect irradiation damage, and so a key knowledge gap regarding each of these was identified. Specifically: (1) What factors affect the ballistic dissolution susceptibility of different solute nanocluster species? (2) Over the fusion-relevant temperature range, how do phase instabilities contribute to hardening and embrittlement in ODS alloys? and (3) For ODS alloys, how does high dose neutron exposure affect the phase stability of nanodispersoids? The specific materials and methods used for experiments are detailed in Chapter 3. Then in Chapters 4 – 6 the research questions are addressed in sequence. Finally, in Chapter 7, key perspectives on irradiation phase stability in nuclear structural steels uncovered during this work are highlighted.

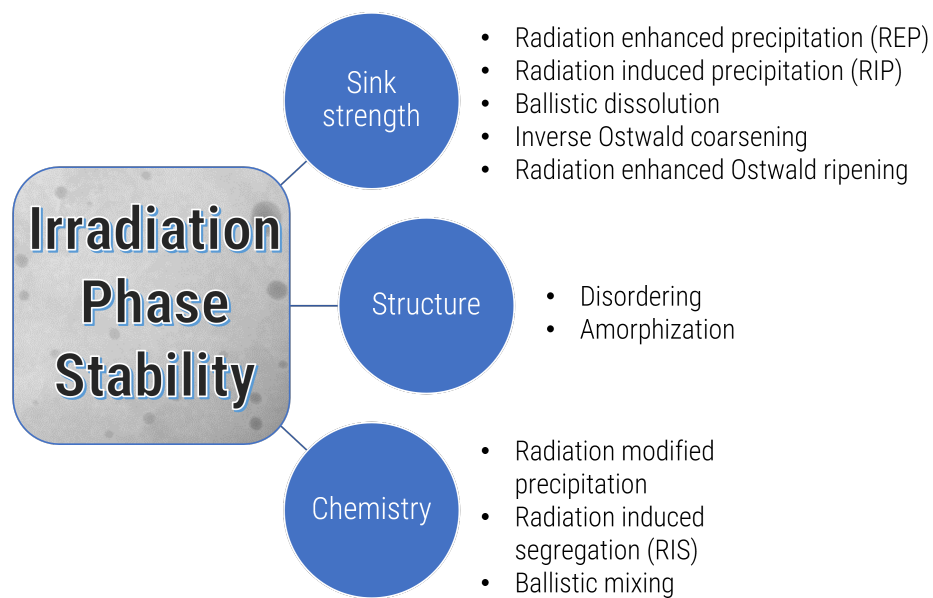


Figure 1.2: A diagram showing the various processes that may contribute to irradiation phase stability

Chapter 2

Literature Review

2.1 General radiation damage theory

2.1.1 Primary damage event

An irradiating particle can be slowed in a material by transferring energy through collisions to lattice atoms. If sufficient energy is imparted, a lattice atom may be displaced from its site. Thus, displacement irradiation damage caused by nuclear energy loss depends on the initial energy of the irradiating particle, the probability of energy transfer described by an energy transfer cross-section, and the number of displacements generated.

The initial energy, E_i , of the projectile is determined by the irradiation source. For electrons and heavy-ions, mono-energetic beams are possible, however the energy of fission neutrons is a spectrum. The type of irradiating particle will also determine the interaction potential and therefore the energy transfer cross-section. Nonetheless, for all particles, maximal energy transfer occurs during head-on, elastic collisions. For a non-relativistic particle with initial energy E_i , the maximum

possible transfer energy, T_{max} , in a binary collision is given by:

$$T_{max} = \frac{4mM}{(m+M)^2} E_i = \Lambda E_i \quad (2.1)$$

where m is the mass of the impinging particle, M is the mass of the target nuclei, and Λ is the kinematic efficiency factor. Given that neutrons are uncharged, they interact with target nuclei based on a hard sphere potential. The hard sphere energy transfer cross-section is given by:

$$\sigma_{HS}(E_i, T) = \frac{\pi \rho^2}{\Lambda E_i} \quad (2.2)$$

where ρ is the sum of the colliding hard sphere radii. As a result, all energy transfers from 0 to T_{max} are equally probable and the average energy transfer is $T_{max}/2$. On the other hand, electrons and heavy-ions, which are charged, tend to have Coulombic-type interactions. The energy transfer cross-section based on a simple Coulombic potential is given by:

$$\sigma_{Coul}(E_i, T) = \pi Z_1^2 Z_2^2 e^4 \left(\frac{m_1}{m_2} \right) \frac{1}{E_i T^2} \quad (2.3)$$

where Z_1 and m_1 are the atomic number and mass of the projectile, respectively, Z_2 and m_2 are the atomic number and mass of the target atom, respectively, and e is the elementary charge. The probability of energy transfer therefore decreases in proportion with $1/T^2$. Thus, charged particle irradiations produce a high proportion of low-energy recoil atoms.

Depending on the amount of energy transferred from the irradiating particle, an atom in the material may be displaced from its lattice site. The simplest model to describe the number of displacements, ν , expected under irradiation based on hard-sphere interactions is the Kinchin-Pease model [32]. The amount of kinetic

energy required to create a stable defect by knocking an atom from its lattice site beyond the distance it can spontaneously recombine with the vacancy is considered the threshold displacement energy, E_d . By definition then, if the energy transferred to a lattice atom, T , is less than E_d , no displacements will occur. On the other hand, if $T \geq E_d$, at least one atom will be displaced. The displaced atom that receives energy T from the irradiating particle is known as the primary knock-on atom (PKA). The maximum energy the PKA can transfer in subsequent collisions with neighboring atoms (assuming they are the same mass) is $T_2 = T$. Thus, the PKA must have an energy of $T \geq E_d$ to cause additional displacements. In other words, if $E_d \leq T \leq 2E_d$, only a single atom is displaced. While if $2E_d \leq T \leq E_c$, displacement damage can be propagated by the PKA in what is known as a collision cascade. E_c is defined as the cutoff energy, above which it is assumed for simplicity that only electronic energy losses occur. For the n^{th} collision, the average energy transferred is $T_n/2$, and so the number of displacements in a collision cascade can be estimated by $T/2E_d$. For irradiating particles with an initial energy greater than E_c , no displacements are predicted until the particle energy falls below E_c .

Considering realistic interatomic potentials rather than hard-sphere interactions, Norgett, Robinson, and Torrens proposed an additional factor of 0.8 to account for displacement damage efficiency [33]. In addition, since the transition between electronic and nuclear stopping varies smoothly with energy and is not a sharp cutoff, damage energy, E_D , is introduced to describe the energy available for nuclear collisions. The damage energy is simply the transfer energy minus energy losses due to ionization or $E_D = T - E_{ioniz}$. These modifications to the Kinchin-Pease model

constitute the NRT model, which is summarized as follows:

$$\nu(T) = \begin{cases} 0 & \text{for } T < E_d \\ 1 & \text{for } E_d \leq T \leq \frac{0.8E_D}{2E_d} \\ \frac{0.8E_D}{2E_d} & \text{for } T \geq \frac{0.8E_D}{2E_d} \end{cases} \quad (2.4)$$

The NRT model is considered the current international standard for calculating displacement damage. The unit displacements per atom, abbreviated as dpa, is used to quantify irradiation damage, and is calculated for a mono-energetic beam with particle flux ϕ by:

$$dpa_{NRT} = \phi \int_{T_{min}}^{T_{max}} \sigma(E_i, T) \cdot \nu(T) \cdot dT \quad (2.5)$$

Some important limitations of the NRT model are that it does not account for damage due to ionization, transmutation reactions, clustering of defects in-cascade, mixing due to replacement collisions, or recovery due to athermal recombination. Thus, NRT dpa provides a method to quantify irradiation damage, but is not all encompassing. In metals, damage mainly takes the form of isolated Frenkel (vacancy and interstitial) defects and defect clusters. The interactions of these defects and defect clusters with one another and with other atoms in the material are key to understanding the mechanisms of radiation damage.

2.1.2 Radiation enhanced diffusion (RED)

The self-diffusion coefficient, D , which measures the migration of atoms, can be calculated by adding the contribution from each diffusion mechanism. Thus, D is defined by:

$$D = \sum f_j D_j C_j \quad (2.6)$$

where f_j is a factor that accounts for successive migratory jumps that may be correlated to the same defect j . For pure metals, f_j is close to unity. D_j is the diffusion coefficient for a mechanism involving j type defects and C_j is the concentration of j type defects. At thermal equilibrium, diffusion predominately occurs by the vacancy mechanism, and so $D \approx D_v C_v^{eq}$ where C_v^{eq} is the thermal equilibrium concentration of vacancies. C_v^{eq} can be determined by:

$$C_v^{eq} = \frac{1}{\Omega} \exp \left(\frac{-G_v}{k_B T} \right) \quad (2.7)$$

where Ω is atomic volume, G_v is the vacancy Gibbs free energy, k_B is Boltzmann constant, and T is temperature. Assuming vibrational entropy and hydrostatic stress can be neglected, Equation 2.7 simplifies to:

$$C_v^{eq} = \frac{1}{\Omega} \exp \left(\frac{-E_v^f}{k_B T} \right) \quad (2.8)$$

where E_v^f is the formation energy for a single vacancy. Under irradiation, the rigorous creation of point defects can promote the activation of other diffusion mechanisms. For example, diffusion by the interstitial mechanism or by aggregate defects such as di-vacancies may be significant. However, because the formation energies of defect aggregates are often unknown, the self-diffusion coefficient under irradiation, D^{irr} , is usually approximated by the contribution of isolated vacancies and interstitials [34]. Assuming $f_v, f_i \approx 1$, Equation 2.6 simplifies to:

$$D^{irr} = D_v C_v + D_i C_i \quad (2.9)$$

In order to calculate D^{irr} , one first needs to solve for the concentrations of vacancies and interstitials. These values can be estimated at steady state based on rate theory. Assuming there are no point defect concentration gradients:

$$\frac{dC_v}{dt} = G^{irr} + K^{th} - D_v C_v k_v^2 - \alpha C_i C_v \quad (2.10a)$$

$$\frac{dC_i}{dt} = G^{irr} - D_i C_i k_i^2 - \alpha C_i C_v \quad (2.10b)$$

Here G^{irr} is the point defect generation rate under irradiation, K^{th} is the rate of thermal vacancy creation, k_j^2 is the total sink strength for j type defects, and α is the recombination rate, which is estimated by $4\pi(D_i + D_v)/a^2$ (a is the lattice parameter). The term $\alpha C_i C_v$ describes the loss of point defects by mutual recombination, while the terms containing k_j^2 describe loss of point defects to sinks.

At low temperatures ($T \leq 0.25T_m$), the diffusion of point defects to sinks is limited and therefore, the predominant method of defect annihilation is by recombination. The point defect rate equations can thus be simplified by ignoring the sink absorption term and K^{th} . Assuming $D_i \gg D_v$:

$$D^{irr} \approx \sqrt{\frac{G^{irr} D_v a^2}{4\pi}} \quad (2.11)$$

As a result, the activation energy for diffusion under irradiation at low temperatures where recombination is dominant is E_v^m , the vacancy migration energy.

Under sink dominant conditions, the recombination terms of equations 2.10a and 2.10b are negligible. As a result, $D_i C_i \approx G^{irr}/k_i^2$ and $D_v C_v \approx G^{irr}/k_v^2$, and D^{irr} can be estimated by:

$$D^{irr} \approx G^{irr} \left(\frac{k_i^2 + k_v^2}{k_i^2 k_v^2} \right) \quad (2.12)$$

And so, there is no activation energy required for diffusion under sink dominant conditions. At intermediate temperatures, where defects may be lost to both recombination and sinks, the activation energy for diffusion is thus roughly $E_v^m/2$.

Because of the elevated point defects populations generated under irradiation at low and intermediate temperatures, diffusion is enhanced. Specifically, radiation enhanced diffusion (RED) occurs when $D_v C_v^{eq} \ll D_v C_v + D_i C_i$. At high temperatures, there is no enhancement in diffusion as C_v^{eq} is much higher than the concentration of vacancies produced during irradiation, C_v^{irr} . In this temperature regime, diffusion relies almost entirely on the vacancy mechanism, and so the activation energy is simply $E_v^f + E_v^m$.

2.1.3 Radiation induced segregation (RIS)

Radiation induced segregation (RIS) consists of non-equilibrium micro-chemical alterations driven by point defects fluxes to sinks. At 30 to 60% of a material's melting temperature, RIS is a significant factor, since point defects are readily mobile [35].

Which solutes enrich or deplete at a defect sink depends strongly upon the nature of point defect-solute flux couplings. Three coupling mechanisms exist for a simple A-B alloy. The first is known as the inverse Kirkendall mechanism. If fluxes of A and B are both opposite to the vacancy flux, the element with faster diffusion will deplete, while the element with slower diffusion will enrich. Another possible RIS mechanism is vacancy drag. If either A or B is strongly bound to vacancies, that solute species will be dragged towards the sink and will be enriched. Similarly, the last RIS mechanism is interstitial drag, where if both A and B bind with interstitials, the faster diffusing element will enrich the sink. A complication is that these different RIS mechanisms are not mutually exclusive, and therefore it is often difficult to predict RIS in an alloy system.

Attempts to model RIS have been made using the thermodynamics of irreversible processes (TIPs) [35]. Consider a material with diffusing species β , where β may be either vacancies (v), interstitials (i), or a solute species. In this system, the flux of any particular species α , J_α , is given by:

$$J_\alpha = - \sum_{\beta} L_{\alpha\beta} X_\beta \quad (2.13)$$

where $L_{\alpha\beta}$ is the Onsager or kinetic coefficient and X_β is the driving force for the diffusion of species β equivalent to the gradient of chemical potential for species β . In principle, the off-diagonal Onsager coefficients, where $\alpha \neq \beta$, give valuable insight into the coupling effects between diffusing species [36]. Unfortunately, it is extremely difficult to measure values of the Onsager coefficients in practice.

2.1.4 Precipitation under irradiation

Precipitate phases may exist in a material under thermal equilibrium conditions, assuming both sufficient thermodynamic driving force and adequate kinetics exist. The production of point defects by irradiation, however, creates a non-equilibrium environment and allows for RED of solute atoms. As a result, precipitation pathways may be introduced or modified.

Radiation enhanced diffusion can promote the formation of phases that are stable at thermal equilibrium, but are normally kinetically inhibited [37]. Such a process is known as radiation enhanced precipitation (REP). Elevated concentrations of point defects increase the solute diffusion coefficient, but the thermodynamics of the system remain fundamentally unchanged. Because REP phases are thermally stable, they cannot be dissolved by thermal aging at or below the irradiation temperature at which they were formed. Key examples of REP include Cu-rich precipitates in RPV steels [38] and α' precipitation in ferritic steels [39].

In addition to RED, solute-point defect flux couplings can support phases that are not thermally stable. Such radiation induced precipitation (RIP) phases will dissolve during post-irradiation annealing, and therefore are reversible. RIS at defect sinks (cavities, grain boundaries, dislocation lines, etc.) can cause a supersaturation of solute atoms in a localized area, which leads to heterogeneous nucleation. Defect sinks are not a prerequisite for RIP though, as homogenous nucleation can occur if Frenkel pair recombination is enhanced in solute rich regions [40, 41]. A classic example of RIP is γ' in Ni-Si alloys [34].

The last type of precipitation that can occur in irradiated materials is radiation modified precipitation. Solute point-defect flux couplings can produce “micro-alloy” environments, which are defined as localized areas in an alloy that deviate from the original composition [42]. Radiation modified phases are thermally stable at the original alloy composition, but the aforementioned “micro-alloy” environments can enhance nucleation and growth, retard nucleation and growth, or change the chemistry of the phases. The phases that form under irradiation are therefore a reflection of the “micro-alloy” environment rather than the original alloy composition. For example, in 316 austenitic stainless steel, the $M_{23}C_6$ phase, which is Ni and Si poor, has been observed to be retarded under irradiation while the Laves phase, which is Ni poor and Si rich, showed enhanced formation with increased Ni content [42].

2.1.5 Ballistic mixing

Unique to the radiation environment, ballistic mixing can rearrange atoms such that phases are disordered or dissolved. In this section, we will restrict our discussion to ballistic (recoil) dissolution, which can result in changes in precipitate size and number density under irradiation, and radiation induced amorphization.

Recoil dissolution

Ballistic mixing can cause solute atoms to be ejected from a precipitate and deposited nearby into the matrix. On the other hand, RED can supply the precipitate with a flux of incoming solute atoms. Because RED and ballistic mixing are counteracting, the size stability of phases under irradiation, to a first approximation, is a balance of these two processes. In general, a precipitate will grow if the solute flux from RED exceeds the ballistically ejected solute flux. For a spherical precipitate, at steady state:

$$D_s^{irr} \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial C}{\partial r} \right) = \phi W(\delta) \quad (2.14)$$

D_s^{irr} is the irradiation enhanced chemical diffusion coefficient for solute s , r is radial distance from the center of the precipitate, C is solute concentration, ϕ is the bombarding particle flux, δ is radial distance from the precipitate interface, and $W(\delta)$ is a function describing the spatial probability distribution of solute atoms displaced out of the precipitate [43]. The LHS of equation 2.14 represents the change in solute concentration due to incoming RED flux, and the RHS represents the change in solute concentration due to the outgoing ballistic flux.

Assuming an exponential recoil distribution, Heinig et al. derived the following expression for $W(\delta)$ for a spherical precipitate where a solute atom is isotropically displaced by a recoil [43]:

$$W(\delta) = \frac{q\lambda \exp\left(\frac{-(\delta+r_0)}{\lambda}\right)}{2r(\delta+r_0)} \times \left[\left(\frac{r_0(\delta+r_0)}{\lambda^2} + \frac{3r_0}{\lambda} \right) \cosh(r_0/\lambda) - \left(\frac{r_0^2}{\lambda^2} + \frac{r_0}{\lambda} + 3 \right) \sinh(r_0/\lambda) \right] \quad (2.15)$$

where r_0 is precipitate radius, q is the ballistic mixing rate and λ is the mean atomic displacement distance.

An important implication of equation 2.14 is that irradiation may modify $C(r)$. Under thermal conditions, one boundary condition for $C(r)$ is $C(\infty) = C_0$, where C_0 is the bulk concentration of solute, while the other boundary condition is the solute concentration at the interface, given by the Gibbs-Thomson equation:

$$C(r_p) = C_\infty \left(1 + \frac{2\gamma V_m}{R_g T r_0} \right) \quad (2.16)$$

C_∞ is the equilibrium solute concentration at a flat interface (equivalent to the solubility limit), γ is the interfacial energy, V_m is the molar volume of the precipitate phase, R_g is the universal gas constant, and T is temperature. Commonly, $2\gamma V_m / R_g T$ is defined as the capillary radius, r_c .

Combining equations 2.14 and 2.15, Heinig et al. showed that under irradiation both C_∞ and r_c can be modified [43]. For a precipitate with radius r_p , the solute concentration at the interface, $C^{irr}(r_p)$, considering ballistic effects, is thus given by:

$$C^{irr}(r_p) = C_\infty^{irr} \left(1 + \frac{r_c^{irr}}{r_p} \right) \quad (2.17)$$

where C_∞^{irr} is the irradiation modified equilibrium solute concentration at a flat interface and r_c^{irr} is the irradiation modified capillary radius calculated by:

$$r_c^{irr} = \frac{r_c - 5\lambda\Delta/4}{1 + \Delta} \quad (2.18a)$$

$$C_\infty^{irr} = C_\infty(1 + \Delta) \quad (2.18b)$$

$$\Delta = \frac{q\phi\lambda^2}{D_s^{irr}C_\infty} \quad (2.18c)$$

The irradiation modified capillary radius gives an indication of how the precipitate distribution is expected to change under irradiation. For $r_c^{irr} > 0$, conventional Ostwald ripening is expected, while for $r_c^{irr} < 0$ inverse Ostwald ripening is predicted.

The analytical solutions for r_c^{irr} and C^{irr} given by equations 2.18a and 2.18b are obtained disregarding solute atoms dissolved close (≤ 1 nm) to the precipitate interface. In addition, the Heinig model does not consider ballistic transport of solute atoms from the matrix to the precipitate. Phase field models that include these effects further predict that ballistic dissolution rather than inverse coarsening of the precipitates will occur if the displacement of solute atoms is less than a critical relocation distance, R_c [44, 45]. For an equi-atomic immiscible binary alloy, $R_c \approx a_0$, where a_0 is the lattice parameter. While, this may seem like a low threshold value, it is comparable to the effective relocation distance of solutes during heavy ion and neutron irradiation [46]. Thus, ballistic dissolution of precipitates has been commonly observed under these irradiation conditions.

Radiation induced amorphization

Ballistic mixing may also cause disordering of ordered structures. For ceramics and intermetallics, another possible consequence is the complete loss of long-range structure, referred to as radiation induced amorphization (RIA).

The process of RIA is generally described either by using a direct-impact model or a defect accumulation model. In the direct-impact model, amorphous regions are formed in the core of the displacement cascades [47]. Heavy ions, because of their dense cascades, are assumed to predominantly cause amorphization by direct impact [48]. With this mechanism, the amorphous fraction of material increases exponentially with ion dose until no crystalline regions remain.

In contrast to direct-impact, the defect accumulation model suggests that amorphous domains form after a critical concentration of defects is attained. With electron irradiation, damage accumulation can occur homogeneously until the lattice is destabilized. For cascade producing irradiation (i.e. ion and neutron irradiation), the amassing of defects may occur when successive impact events affect the same

volume [47, 48]. Amorphization therefore occurs heterogeneously. Because the probability of a cascade overlapping with a previously damaged region increases with dose, RIA progresses in a sigmoidal manner.

Gibbons provides the following equation to predict the amorphous volume fraction, F_{am} , in an irradiated material [49]:

$$F_{am} = 1 - \sum_{i=0}^{n-1} \frac{(a\phi t)^i}{i!} [-\exp(-a\phi t)] \quad (2.19)$$

where a is the damage cross section for disordering and amorphization, ϕt is the ion fluence, and n is the number of cascade overlaps required for amorphization. Thus, Equation 2.19 can be used to model the kinetics of direct-impact damage for low energy heavy ions by setting $n = 1$ or defect accumulation by cascade overlap for higher energy or lighter ions by setting $n \geq 2$.

Above a certain temperature, a material readily recovers from irradiation induced damage, and amorphization does not occur. However, this critical amorphization temperature, T_c , depends on the irradiating particle. Since electron irradiation produces isolated Frenkel pairs, the critical amorphization temperature for electron irradiations is closely related to the onset of interstitial migration. For heavy-ion irradiations, local damage rates in a cascade are much higher compared to isolated Frenkel pair production, and so the damage is more difficult to anneal. Thus, the critical amorphization temperature for heavy-ion irradiations is higher than for electron irradiations. Further, as ion mass increases, T_c increases as well since deposited energy density is higher for heavier ions. The critical amorphization temperature for neutron irradiations is typically slightly lower than for heavy-ion irradiations. In most cases, the damage rates for neutron irradiations are several orders of magnitude lower than for heavy-ion irradiations, and so there is more time in between cascade events for damage to anneal [50].

Despite abundant research, the factors that determine a material’s susceptibility to RIA are poorly understood. For example, the critical amorphization temperatures of various perovskites during 800 keV Kr⁺ irradiation has been shown to widely vary between 152 °C and 607 °C [51]. Some of the proposed criteria for amorphization susceptibility include melting temperature, bond ionicity, structural distortion, and structural freedom [52, 53, 54, 55]. Wang et al. have attempted to quantify amorphization susceptibility based on structural connectivity, bond strength, and thermodynamic stability with a parameter S [52]. Even though it includes multiple factors, the parameter S still fails to accurately predict the behavior of some systems, which suggests that additional refinement of amorphization susceptibility criteria is needed.

2.1.6 Radiation hardening and embrittlement

Because of defects produced during irradiation, materials experience radiation hardening and embrittlement. Hardening contributions can come from a range of features including point defects, point defect clusters, He bubbles, solute clusters, dislocation line and loops, stacking fault tetrahedra (SFT), cavities, and precipitates. Each of these features produce hardening by acting as obstacles to dislocation motion. For strong barriers, the dispersed barrier hardening (DBH) model introduced by Seeger can be used to estimate change in yield strength, $\Delta\sigma$ [56]:

$$\Delta\sigma = M\alpha\mu b\sqrt{Nd} \quad (2.20)$$

where M is the Taylor factor (3.06 for equiaxed face-centered and body centered cubic materials [57]), α is barrier strength, μ is the shear modulus, b is the Burgers vector of the glide dislocation ($a/2 < 111 >$ in bcc Fe alloys with $a = 0.287$ nm), N is the defect number density, and d is the diameter of the defects. Values for α typically

vary from 0.1 up to 1 for Orowan hardening. Voids and large precipitates normally are strong obstacles with $\alpha \approx 1$; dislocation loops, small precipitates, and He bubbles tend to be intermediate strength obstacles with $\alpha \approx 0.4$; and solute clusters, small bubbles, SFTs, and dislocation lines are likely weak obstacles with $\alpha < 0.25$ [58, 59]. When approximating the change in yield strength due to weak obstacles ($\alpha < 0.25$), the Friedel–Kroupa–Hirsch (FKH) model is often more appropriate, since the force from the obstacles is distributed uniformly along the interacting dislocation line rather than localized at certain points [60, 61]:

$$\Delta\sigma = M\alpha\mu b d N^{2/3} \quad (2.21)$$

Most irradiated microstructures contain multiple sources of hardening, and their effects must be appropriately combined. First, root mean square (RMS) superposition can be used to assess the hardening contribution of obstacles with similar barrier strength. Then, linear superposition can be used to combine the effects of weak and strong obstacles. For example, in non-irradiated oxide dispersion strengthened steels, Massey et al. found good agreement with measured yield strength by combining the effects of grain boundaries (σ_{gb}), carbonitrides (σ_{Or}), dislocation forest hardening (σ_d), solid solution hardening (σ_s), and nanoclusters (σ_{db}) with [62]:

$$\sigma_y = \sqrt{\sigma_{gb}^2 + \sigma_{Or}^2 + \sigma_d^2} + \sqrt{\sigma_s^2 + \sigma_{db}^2} \quad (2.22)$$

In addition to hardening, in irradiated body-centered cubic (bcc) materials there is embrittlement. Specifically for impact toughness, the ductile-to-brittle transition shifts to higher temperatures, and there is a loss in upper shelf energy [63, 64]. Values for impact toughness are of interest since they are generally correlated to fracture toughness, or the material’s ability to resist propagation of an existing flaw. In

addition, change in yield strength can be roughly estimated by the change in ductile-to-brittle transition temperature (DBTT) by a Ludwig-Davidenkov relationship [23].

2.2 Radiation damage in austenitic stainless steels

2.2.1 Radiation induced segregation in AuSS

For type 304 and 316 stainless steels, the temperature range where RIS is significant is approximately 420 to 700 °C. It is well known that in simplistic Fe-Cr-Ni alloys, nickel, which diffuses most slowly, will enrich and chromium, which diffuses most quickly, will deplete at the grain boundaries. Whether iron enriches or depletes tends to be a function of the alloy's bulk composition.

In the past, two mechanisms were proposed for RIS in Fe-Cr-Ni alloys; the first being the inverse-Kirkendall effect involving a vacancy flux and the second being the formation of defect-solute complexes. Allen has since provided evidence that the inverse Kirkendall effect is the primary mechanism by which RIS occurs in austenitic Fe-Cr-Ni alloys [65]. After analyzing RIS profiles in seven different proton-irradiated Fe-Cr-Ni alloys, Allen demonstrated that the diffusivity ratio between chromium and iron follows trends indicative of high temperature diffusion, as would be the case if segregation is being governed by vacancies. The experimental results did not support interstitial binding behavior, since the observed concentrations of nickel and iron were lower than predicted under defect-solute complex models. In conjunction with his findings, Allen updated the Perks model, which predicts RIS based on atom-vacancy jump-rates, to account for composition dependent migration energies and short-range ordering effects. For austenitic alloys, the attraction between nickel and chromium atoms must be taken into consideration since it reduces the segregation of both elements. The modified inverse Kirkendall (MIK) model,

therefore, incorporates solute pair interaction energies to more accurately predict grain boundary concentrations.

In 300 series stainless steels, minor alloying elements may also undergo radiation induced segregation. Manganese and molybdenum both deplete at grain boundaries under irradiation because they are rapid diffusers [66]. In addition, some fluxes of minor alloying elements are caused by mechanisms alternative to the inverse Kirkendall effect. Most notably, silicon, which is undersized, segregates by the interstitial binding mechanism [67]. There are some alloying elements that exhibit even more complex behavior. Though carbon migrates by way of interstitials, a study by Jiao and Was [68] has shown evidence using atom probe tomography of carbon depletion at grain boundaries. Jiao and Was hypothesized that carbon may co-segregate with chromium. Inconsistently, phosphorous enrichment at grain boundaries has also been reported, suggesting that thermal segregation of phosphorous may be enhanced by irradiation. The RIS behavior for other elements such as boron, nitrogen, and sulfur has not been established.

Besides at grain boundaries, RIS has also been observed at voids and dislocations in austenitic stainless steels. Hishinuma et al. [69] analyzed 316 stainless steel and other Fe-Ni-Cr alloys irradiated in a high voltage electron microscope with 1 MeV electrons between the temperatures 350 and 600 °C to a dose of approximately 30 dpa and found coated voids. Energy dispersive spectroscopy indicated that the void surfaces were nickel enriched. Using more recent and sophisticated technology, researchers have been examining the clustering of solutes. For instance, atom probe tomography work by Etienne et al. [70] focused on determining whether Ni-Si clusters could be correlated to dislocation loops in 15% cold-worked 316 stainless steel irradiated at 350 °C to 10 dpa with 10 MeV Fe⁵⁺ ions. Indeed, the torus and rounded solute clusters detected matched with the size and density of dislocation loops previously observed by TEM.

2.2.2 Precipitates under irradiation in AuSS

The enhancement, retardation, modification, or inducement of precipitates in the radiation environment is strongly associated with RIS. Not surprisingly then, precipitation predominately occurs in austenitic stainless steels from 300 to 800 °C, the temperature range where RIS is pervasive. Ascribing a particular dose as to when radiation-produced precipitation occurs is more difficult. Zinkle et al. [4] have suggested that the precipitate microstructure may not reach “steady-state” until at least 50 dpa. Fig. 2.1 presents a compilation of experimental results for solution annealed 316 steel irradiated in fast reactors, demonstrating the array of temperatures and doses where precipitates have been observed.

Theoretically, RIS and homogeneous radiation induced precipitation should be delayed by the presence of cold work. Since existing network dislocations act as sinks, overall point defect fluxes are reduced and, as a result, solute mobility is hindered in cold worked materials during the early stages of microstructure evolution. However, experimentally, the effect of cold work on grain boundary RIS is barely perceptible, especially after ~ 1 to 2 dpa [71, 72]. This is likely because grain boundaries have a high sink strength compared to network dislocations. By contrast, it has been experimentally observed [73] that there is a delay to homogeneous radiation induced precipitation by cold work since the sink strength of network dislocations is unopposed by other pre-existing interfaces. Heterogenous nucleation, alternatively, has been observed to be enhanced because network dislocations serve as preferential nucleation sites [73, 74].

The precipitates found in irradiated 300 series austenitic stainless steels can be subdivided into three categories: radiation enhanced or retarded, radiation modified, and radiation induced (Table 2.1). Radiation enhanced or retarded phases (M_6C , Laves, $M_{23}C_6$, MC, σ , and χ) are phases that occur like they would with thermal aging, but in an altered quantity. Since they are thermodynamically stable, these

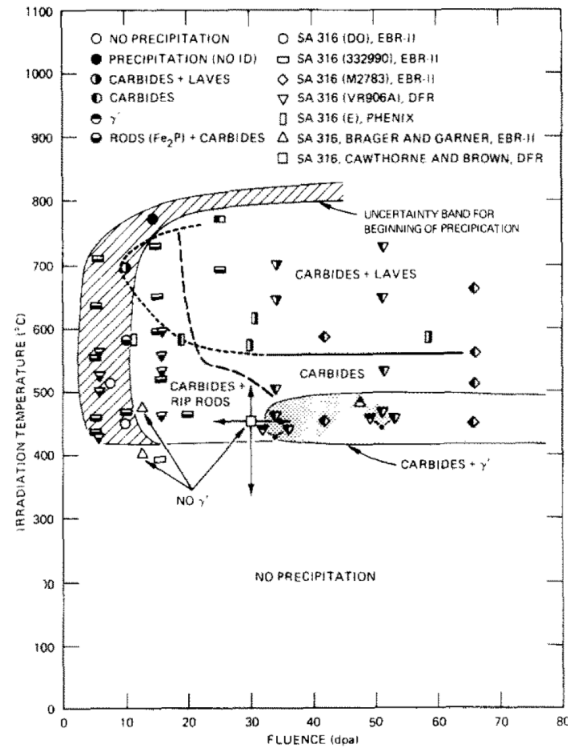


Figure 2.1: Map of precipitate formation in fast reactor irradiated, solution annealed 316 stainless steels as a function of irradiation temperature and dose. Reprinted from [4].

precipitates remain after post-irradiation annealing. In contrast, radiation-modified phases (M_6C , Laves, and M_2P) have a composition that differs from when they are produced via thermal aging. Finally, radiation-induced phases ($M_6Ni_{16}S_7$ (G), Ni_3Si (γ'), MP, M_2P , M_3P) are phases that do not normally form under thermal aging. Given their instability, radiation-induced phases will dissolve during post-irradiation annealing. In general, the presence of radiation modified or induced phases during irradiation at 450 to 600 °C is indicative of poor radiation resistance, whereas the presence of radiation enhanced or retarded phases suggests the opposite [4].

Normally, the composition of radiation-modified phases follows the trends of RIS. Yang [75] reported that in 316 stainless steel irradiated in EBR-II, Laves phase was enriched in nickel and depleted of molybdenum compared to Laves formed by thermal aging. In addition, the composition of both M_6C and Laves phase was altered such that the molybdenum content increased and the nickel content decreased with increasing temperature. Thus, as temperature increased, thermal effects strengthened, RIS effects diminished, and radiation-modified phases more closely resemble their thermally aged counterparts.

The formation of G and γ' phase in 300 series stainless steels is unique to the radiation environment. G phase is face-centered cubic with a composition of $M_6Ni_{16}Si_7$. For 316 stainless steel, M atoms are typically Mn, Cr, and less frequently, Fe, and Mo [73]. There is a strong correlation between G phase precipitation and void formation. Lee and Mansur [1] observed in irradiated Fe-Ni-Cr alloys that the relationship between cavity size and precipitate size was linear. They submit that the point defect collector mechanism can explain the growth of precipitate-cavity pairings. According to this mechanism, point defects are first trapped at the matrix-precipitate interface and then continue to move along the interface as if at a grain boundary. Eventually, the point defects reach an attached cavity where they are

Table 2.1: Common precipitate phases in austenitic stainless steels. Reprinted from [1].

Phase ¹	Crystal Structure	Lattice Parameter (nm)	Atoms/Unit Cell	Typical Morphology	Orientation to Matrix
γ (TP)	cubic, $A1$, $Fm3m$	$a_0 = 0.36$	4	matrix	—
γ' (RI)	cubic, $L1_2$, $Fm3m$	$a_0 = 0.35$	4	small sphere	cube-on-cube
G (RI)	cubic, $A1$, $Fm3m$	$a_0 = 1.12$	116	small rod	random
Laves (RM)	hex., $C14$, $P6_3/mmc$	$a_0 = 0.47$ $c_0 = 0.77$	12	faulted lath	many variants
$M_{23}P$ (RM)	hex., C_{22} , P_{321}	$a_0 = 0.604$ $c_0 = 0.36$	6	thin lath	$(1\bar{2}10)ppt// (011) \gamma$ $0001)ppt// (001) \gamma$
MC (RE)	cubic, $B1$, $Fm3m$	$a_0 = 0.433$	8	small sphere	cube-on-cube
η (RE)	cubic, $E9_3$, $Fd3m$	$a_0 = 1.08$	96	rhombohedral	cube-on-cube or twin
σ (RE)	tet., $D8_b$, P_4/mnm	$a_0 = 0.88$ $c_0 = 0.46$	30	various	many variants
$M_{23}C_6$ (TP)	cubic, $D8_4$, $Fd3m$	$a_0 = 1.06$	92	rhombohedral platelet	cube-on-cube or twin
X (TP)	cubic, $A12$, $1\bar{4}3m$	$a_0 = 0.89$	58	various	many variants
TiO (TP)	cubic, $B1$, $Fm3m$	$a_0 = 0.425$	8	small rod	—
Cr_2O_3 (FP)	hex., D_{51} , $R\bar{3}c$	$a_0 = 0.495$ $c_0 = 1.358$	30	globular	—
SiO (FP)	—	—	—	globular	—
ZrO (FP)	cubic, $B1$, $Fm3m$	$a_0 = 0.46$	8	globular	—
NbO (FP)	cubic, $B1$, $Fm3m$	$a_0 = 0.427$	8	globular	—
TiN (FP)	cubic, $B1$, $Fm3m$	$a_0 = 0.425$	8	large cuboid	—
MxSy (FP)	many stoichiometric relations				

¹ TP = thermal phase; RI = radiation induced; RM = radiation modified; RE = radiation enhanced; FP = fabrication product

absorbed. Thus, cavities paired with precipitates have a higher sink strength than isolated cavities and an accelerated growth rate.

γ' is another radiation-induced precipitate phase, which normally forms alongside dislocations. Like G phase, γ' is face-centered cubic and nickel and silicon rich. In austenitic stainless steels, it has a composition of Ni_3Si . Compared to G phase, γ' forms over a wider temperature range. In 316 stainless steel with ≤ 1 wt% Si, γ' has been observed in samples irradiated in fast breeder reactors at temperatures as low as 270°C and as high as 575°C . The size of γ' particles which is normally between 5 and 15 nm is sensitive to composition and thermomechanical processing [73]. Not surprisingly, factors which increase the dislocation density decrease the size and increase the abundance of γ' precipitates. Additions of silicon and phosphorus in austenitic stainless steels, which increase the density of dislocation loops, and cold-work, which increases the network dislocation density, increase the number of nucleation sites for γ' precipitation. The result is an elevated density of fine particles in these materials [1].

As both G and γ' phase form due to solute segregation, the presence of helium, which modifies RIS behavior, can affect their formation. Helium leads to the creation of bubbles that serve as neutral sinks and, by extension, recombination centers for point defects. Thus, helium reduces RIS and the concentration gradients that result in radiation-induced precipitation [73]. Maziasz [76] recognized this behavior when comparing the precipitates formed in one heat of cold-worked 316 stainless steel irradiated in both EBR-II and HFIR at 500 to 550°C and a dose of 61 to 69 dpa. G and γ' phase formed more readily in the sample irradiated in EBR-II than in HFIR where helium levels were 41 appm and 3660 appm, respectively.

2.3 Radiation damage in ODS alloys

2.3.1 Non-irradiated microstructure and mechanical properties of ODS

Alloy fabrication

ODS alloys contain pre-existing secondary phase particles. The initial number density and size distribution of the oxides greatly depends on manufacturing. Unlike commercial ferritic/martensitic steels, ODS alloys are fabricated through powder metallurgy rather than by traditional melt methods [77]. In the first step of manufacturing, mechanical alloying (MA) of metal and oxide powders is performed with high-energy ball milling in an argon gas atmosphere. While severe deformation causes the metal powders to form a solution, the inert oxide powder may either dissolve into solution [78, 79, 80] or remain as unmixed fragments [77, 81, 82]. Oxide particle size decreases as milling time increases, although it eventually saturates when there is dynamic equilibrium between fracture and welding rates [82]. After MA, the resulting powder mixture is then consolidated into a dense structure by hot isostatic pressing (HIP) or hot extrusion (typically performed at $\sim 850 - 1150^\circ\text{C}$). If the oxide powder was dissolved during MA, the consolidation time-temperature-process history will significantly affect the clustering and precipitation of the nano-oxides [78, 83, 84]. During consolidation, extrusion produces an anisotropic grain structure, typically consisting of a $\langle 110 \rangle$ -fiber texture with grain aspect ratios of $\sim 2 - 10$ [85]. This results in poor creep strength, ductility, and fracture toughness along certain orientations [84, 85]. As a result, thermomechanical treatments (TMTs) including cold and warm working and static recrystallization are typically used to achieve a more equiaxed grain structure. For nano-structured ODS alloys, most grain sizes are sub-micrometer, although some grains may be as large as $10\text{ }\mu\text{m}$.

[85]. TMTs are also used to shape the alloy into its final geometry, which may be thin-walled cladding tubes or thick-walled structures.

Chemistry and structure of oxides

Besides processing, oxide properties are also a function of alloy chemistry. Yttria (Y_2O_3) is commonly used during MA as the oxide reinforcement because it has excellent thermal stability. In fact, X-ray diffraction studies show that yttria keeps its cubic structure up to around 2239°C [86]. When alloy fabrication is complete, the diameter of these Y_2O_3 oxides is $\sim 10 - 50$ nm [87, 88, 89]. As a result, titanium is commonly added to refine the distribution of the oxides. The average oxide diameter is reduced to ~ 3 nm when Ti is added [89]. This effect is believed to be due to the fact that Ti restricts the coarsening of the oxides [90]. It has also been proposed based on ab-initio modelling that Ti increases the binding energy of Y–O–vacancy clusters, which may increase nucleation rate and enable fine oxide dispersions [91]. In addition to Ti, there is evidence that Cr, Zr, and Hf may also reduce the size of the oxides [92, 93, 94].

For fuel cladding applications in supercritical pressurized water and lead-cooled reactors, aluminum is used as an additive to improve coolant compatibility [95, 96]. However while it offers corrosion resistance, aluminum promotes the formation of coarse Y–Al–O dispersoids, which degrade the high temperature strength of the alloy [96, 97]. To prevent this, Zr or Hf, which both have more negative oxide formation energies than Al, may be included along with Al to maintain a high density of fine dispersoids [96, 98, 99, 100].

As was just alluded to, alloy composition not only affects oxide size and number density, but also determines the structure and chemistry of the oxides. The chemistry and crystal structure of possible oxides discussed herein are compiled in Table 2.2. In ODS alloys free of Ti and Al additions, oxides are usually cubic

Y_2O_3 [79, 101, 92, 102]. For ODS alloys containing Ti, the smallest particles appear to be non-stoichiometric oxides (sub-oxides) or possibly Guinier–Preston (GP) zones [103, 104, 85]. As particle size increases, the oxides are more likely to be stoichiometric oxides such as $\text{Y}_2\text{Ti}_2\text{O}_7$ (pyrochlore structure), Y_2TiO_5 , and, to a lesser extent in ferritic ODS steels, YTiO_3 [92, 104, 105].

Al has a lower oxide formation energy compared to Ti [96], and so the oxides that form preferentially when Al is present tend to be either cubic- $\text{Y}_3\text{Al}_5\text{O}_{12}$ (YAG), orthorhombic- YAlO_3 (YAP), monoclinic- $\text{Y}_4\text{Al}_2\text{O}_9$ (YAM), and/or hexagonal- YAlO_3 (YAH) [83, 106, 107, 108]. Out of these phases, YAG is considered to be thermodynamically stable [109] while the other phases may form as intermediates during mechanical alloying [110, 111, 112]. Due to the metastability of YAP, YAM, and YAH, high consolidation temperatures can lead to oxide structural transformations. For example, in a study by Dou et al., YAP formed preferentially over YAH as consolidation temperature increased from 1050 to 1150 °C [83].

Non-irradiated mechanical properties

ODS alloys offer impressive tensile strength. Because the high density of nanodispersoids act as pinning points for dislocation glide, an improvement in tensile strength is seen over non-ODS counterpart steels [113]. For example, the yield strength of ODS-EUROFER is about 35% higher than conventional EUROFER from room temperature to 700 °C [114]. Besides Orowan strengthening from the nanodispersoids, fine grains also provide strengthening through the Hall-Petch effect. These two contributions along with forest dislocation hardening can largely account for tensile stresses observed from room temperature up to about 400 °C [115]. Despite having higher strengths than RAFM steels, some ODS alloys can also maintain acceptable ductility. At room temperature, uniform elongation strains

Table 2.2: Common complex oxides in ODS steels. Crystallographic data compiled from the Inorganic Crystal Structure Database (ICSD).

Formula	Crystal System	Space Group	a (Å)	b (Å)	c (Å)	Atomic Fraction	ICSD Entry
Y ₂ O ₃	cubic	$Ia\bar{3}$ [206]	10.60	10.60	10.60	Y _{0.4} O _{0.6}	23811
Y ₂ Ti ₂ O ₇	cubic	$Fd\bar{3}m$ [227]	10.09	10.09	10.09	Y _{0.18} Ti _{0.18} O _{0.64}	14242
Y ₂ TiO ₅	orthorhombic	$Pmna$ [62]	10.35	3.70	11.25	Y _{0.25} Ti _{0.13} O _{0.63}	34692
YTiO ₃	orthorhombic	$Pmna$ [62]	5.32	5.68	7.61	Y _{0.2} Ti _{0.2} O _{0.6}	8150
YAlO ₃	orthorhombic	$Pmna$ [62]	5.18	5.33	7.37	Y _{0.2} Al _{0.2} O _{0.6}	99419
YAlO ₃	hexagonal	$P6_3/mmc$ [194]	3.68	3.68	10.52	Y _{0.2} Al _{0.2} O _{0.6}	27100
Y ₃ Al ₅ O ₁₂	cubic	$Ia\bar{3}d$ [230]	12.00	12.00	12.00	Y _{0.15} Al _{0.25} O _{0.6}	93634
Y ₄ Al ₂ O ₉	monoclinic	$P2_1/c$ [14]	7.38	10.47	11.13	Y _{0.27} Al _{0.13} O _{0.6}	63650

of $\sim 2 - 20$ % and total elongation strains of $\sim 5 - 30$ % have been reported [116, 113, 114, 7, 84].

By $\sim 550^\circ\text{C}$ at a strain rate of $\sim 10^{-3}\text{s}^{-1}$, deformation fully transitions from athermal dislocation glide to power law creep [85]. Similar to how nanodispersoids act as obstacles to dislocation glide, they also may restrict grain boundary movement. Zener pinning of grain boundaries by oxide particles occurs at high temperatures (up to $\sim 1250^\circ\text{C}$), which retards recrystallization and grain growth [117, 118]. ODS alloys also maintain acceptable strength above $\sim 650^\circ\text{C}$, since deformation requires dislocation climb over hard (unshearable) nano-oxides [115, 117, 119, 120]. As a result, ODS alloys have excellent thermal creep properties [113]. For the best ODS alloys, creep rupture strengths are nearly triple conventional F/M steels, while creep rupture lifetimes are about 1000 times higher [6]. Thus, based on thermal creep properties, ferritic ODS steels may be able to support reactor operating temperatures as high as $750 - 800^\circ\text{C}$.

Poor fracture toughness, which results in a high ductile to brittle transition temperature (DBTT) and low upper shelf energy, is the main area of concern for ODS alloys. Since ODS alloys are anisotropic, the orientation of a propagating crack relative to the extrusion or rolling direction is important. In Charpy impact tests, samples where the anticipated direction of crack extension is in the longitudinal (rolling) direction (the TL orientation for plates and the CL orientation for cylindrical bars and tubes) typically have the lowest toughness, since cracks can easily propagate along elongated grain boundaries [85]. For example, values of DBTT and fracture toughness measured for MA957 with samples machined along the CL orientation were 75°C and $55\text{MPa}\sqrt{\text{m}}$, respectively [121]. Coarse oxides and inclusions can also degrade fracture toughness as they act as initiation sites for cleavage micro-cracks. Recent improvements in fracture toughness have been

achieved by controlling processing to ensure fine isotropic grains and inclusion-carbide-free microstructures [122].

Thermal stability of ODS alloys

As discussed in the previous section with the creep properties, nano-oxides pin grain boundaries and limit dislocation climb. Isothermal aging for 24 hours at 1300 °C ($\sim 0.85T_m$), indicates that grain boundary pinning may also prevent significant grain growth [123]. In addition, only partial dislocation recovery is observed. Experimental studies suggest that Y-Ti-O dispersoids remain stable during thermal aging up to 1000 °C [124]. At temperatures > 1250 °C though, coarsening of the dispersoids can occur [125, 123, 117]. There is also some speculation that coarsening at lower temperatures is possible, but may be kinetically limited. For example, oxide coarsening was observed after 10000 h annealing at 750 °C [117].

For ferritic ODS alloys, a key issue at intermediate temperatures is the separation of the bcc-Fe α phase and the Cr-rich α' phase [126]. The binary phase diagram for the Fe-Cr system is given in Figure 2.2a, and it indicates that below ~ 510 °C, there is a large miscibility gap where α' precipitation is anticipated for alloys with 14.5 to 86 wt. % Cr [5]. At equilibrium, precipitates usually contain around 80 wt. % Cr. Importantly, α' precipitation causes hardening and a decrease in toughness. Thus, α' precipitation is sometimes referred to as “475 °C embrittlement” [127]. The majority of the hardening occurs rapidly, within 12 – 120 h, around 475 °C due to homogeneous nucleation of α' [127]. By comparison, precipitate coarsening during long term aging does not significantly add to hardening. It should be noted that in a sub-region of the miscibility gap, α' precipitates by spinodal decomposition rather than by nucleation and growth. However, despite numerous studies, the precise

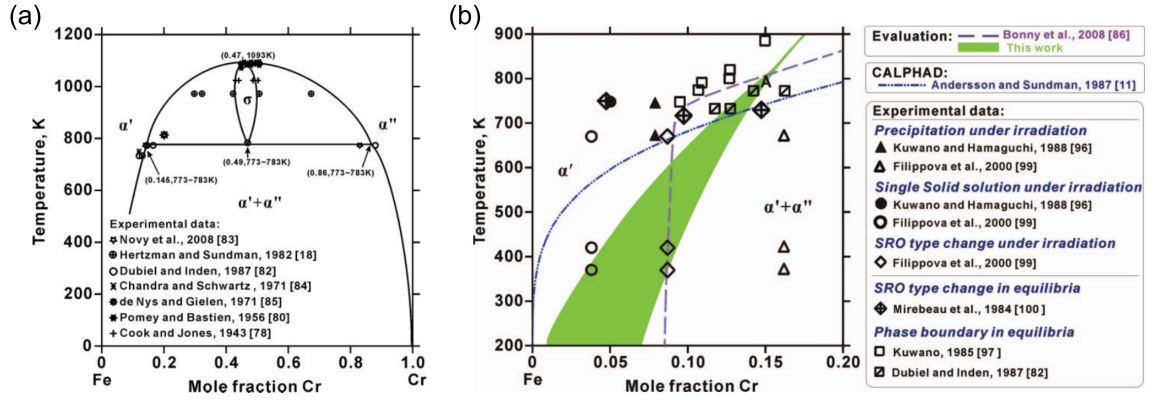


Figure 2.2: (a) A diagram of the Fe-Cr system below 1200 K with supporting experimental results plotted. For clarity, the gamma loop is not shown. (b) A closer view of the Fe-rich side of the Fe-Cr phase diagram between 200 and 900 K. The location of the Fe-solvus line predicted by Xiong et al. [5] is shaded in green. Note: for both (a) and (b), the bcc-Fe phase is denoted as α' and the bcc-Cr phase is denoted as α'' . (a) and (b) are reprinted from [5].

location of both the two-phase boundary, as seen in Figure 2.2b, and the spinodal line remains a topic of debate.

Other solute atoms found in commercial ODS alloys introduce further complications to the thermodynamics and kinetic of Fe-Cr phase separation. Experimentally, additions of Al have been shown to suppress the formation of α' [128, 129]. Although the origin of this effect is not well-understood, Ejenstam et al. have suggested that Al solute atoms screen Cr-Cr interactions in the Fe matrix, and this effectively causes the solubility of Cr to be increased [129]. It has been observed that Ni and Mn additions, on the other hand, accelerate α' formation [130]. Still, the effect of many other solute species remains ambiguous.

2.3.2 Stability of nanodispersoids under irradiation

For nuclear structural material applications, the stability of oxide nanodispersoids under irradiation is a primary concern for ODS alloys. Besides endowing the alloys with impressive high temperature mechanical properties, the particles also act as sinks where the rate of point defect mutual recombination is enhanced [29]. When nanodispersoids are present in high density, the population of freely migrating defects is reduced and the likelihood of extended defect formation is lowered. In addition, ODS nanodispersoids help trap harmful transmutation gases [84, 28], which are expected for steels to be produced at rates around 100 times higher in fusion reactors compared to present fission reactors [131, 132]. Thus, preliminary studies have shown that deleterious cavity swelling in the matrix is reduced in ODS alloys compared to traditional ferritic/martensitic steels (see Figure 2.3) [6].

Unfortunately, literature provides conflicting insights into whether ODS particles are stable during irradiation. This is partially due to the fact that more than one parameter tends to vary between studies. Alloy and oxide composition, irradiating particle, flux, fluence, and temperature all may have effects on experimental

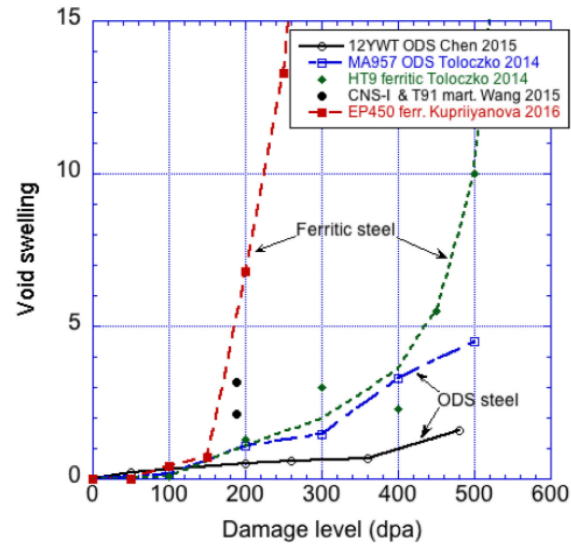


Figure 2.3: A comparison of void swelling with dose in conventional ferritic/martensitic steels and ODS alloys. Data was collected from ion irradiation experiments conducted between 450 and 480 °C. Reprinted from [6].

results. Another issue is that it is challenging to compare studies using different characterization techniques. For example, many APT studies report oxide chemistry, while TEM-based studies do not. To eliminate some confounding variables, we will focus our discussion herein exclusively on neutron irradiation experiments. Table 2.3 provides a summary of the key parameters and results from several neutron irradiation studies.

One of the alloys most frequently examined in the studies listed in Table 2.3 is MA957, a 14Cr ODS variant. Despite numerous studies, the degree to which ballistic dissolution affects the Y-Ti-rich oxides is still unclear. In some studies, such as Refs. [133, 134], no significant changes to the chemistry or size distribution of the oxides are reported. On the other hand, Refs. [11, 135, 136], indicate that some oxides appear to dissolve during neutron irradiation between 287 and 670 °C. Amongst the studies claiming oxide dissolution, it is also disputed whether the small or large particles are most susceptible. In Ref. [137] the size distribution shifted to larger values suggesting radiation enhanced coarsening, while in Ref. [135] the spread of the size distribution narrowed, indicating inverse Ostwald ripening. The different results cannot be clearly ascribed to a temperature effect, as both studies contained samples irradiated ~ 450 °C. However, in a more systematic study, Bailey et al. observed oxide number density decreased with irradiation temperature, suggesting that the ballistic ejection of Y, Ti, and O does occur, but that there is sufficient solute back diffusion that allows oxides to reform at reactor relevant temperatures [136]. Assuming oxide dissolution and reformation occurs cyclically throughout irradiation, this could account for discrepancies between studies, as each experiment only provides an instantaneous result.

The Y-Al-rich nanodispersoids found in alloys DY, MA956, and PM2000 appear to be less stable compared to the Y-Ti-rich oxides. In several neutron irradiation studies, a reduction in oxide number density was reported [138, 139, 140]. For the

one study where no dissolution was reported, the oxides were nonetheless completely amorphized [141]. It appears the Y-Al-rich nanodispersoids may be more unstable relative to the Y-Ti-rich clusters because of their chemistry. Both Refs. [139] and [141] report a loss of Al from the nanodispersoids after neutron irradiation. This is consistent with the fact that Al is more prone to ballistic ejection compared to Ti because of its lower displacement energy [142]. A size effect is unlikely to be the reason why the Y-Al-rich nanodispersoids are more unstable than the Y-Ti-rich clusters. While the Y-Al-rich nanodispersoids are larger and may intercept a higher proportion of collision cascades, there are reports of Y-Ti-rich clusters being stable even at much higher doses (> 100 dpa).

2.3.3 Irradiated mechanical properties of ODS

Similar to RAFM steels, irradiated ODS alloys suffer from irradiation hardening. However, there is no clear trend to indicate whether ODS alloys are systematically better or worse. For example, at ~ 40 dpa, 9%Cr based ODS-Eurofer97 hardens more than Eurofer97 while MA957 hardens less [7]. It has been proposed that ODS alloys may show an improvement against LTBE due to their high sink strength [6]. As discussed earlier, a high density of sinks is expected to increase the rate of point defect mutual recombination, lowering the overall supersaturation of point defects. Figure 2.4 shows above a sink strength of $\sim 5 \times 10^{15} \text{ m}^{-2}$, there appears to be a drop in irradiation induced hardening. However, additional data shown in Figure 2.5 for Fe-Cr and Fe-Cr-Al ODS alloys irradiated in the Japan Materials Test Reactor (JMTR) reveals that initial sink strength effect on LTBE may not be universal [143, 7]. It can be seen that an increase in yield strength (σ_{YS}) was detected in several ODS alloys for irradiation temperatures $> 400 - 450^\circ\text{C}$, where RAFM steels normally see complete recovery. In fact, even as high as 600°C , increased yield strength was retained in a couple of ODS alloys.

Table 2.3: A survey of studies conducted on neutron-irradiated ODS alloys

Alloy	Oxides	Test Reactor	Flux (n/m ² s)	Temp. (°C)	Dose (dpa)	Key Observations	Ref.
MA956	—	FFTF/MOTA	—	418	205	Swelling < 2%, α'	[144]
MA957	—					precipitation, changes to oxides not studied	
F95 ¹	Y ₂ Ti ₂ O ₇ ;	JOYO	—	397	2.5	No significant change to	[145]
	Y-Ti-rich			497	7	the chemistry or	
	clusters			534	15	distribution of the oxides	
DY ²	Ti ₂ O ₃ ;	Phénix	—	435	54.8	Dissolution of fine oxides	[138, 139]
	Y-Al-Ti-rich			484	75.6	for doses > 60 dpa,	
	clusters			508	79.3	re-precipitation around	
				532	78.8	large oxides, loss of Al and	
				580	30.5	Ti in oxides, α'	
						precipitation below 500 °C	
1DS ³	TiO ₂ ; Y-Ti-rich	JOYO	—	450	18	Dissolution of fine oxides	[146]
1DK ⁴	complex oxides			542	17 – 21	with stability more	
				561	10.5	sensitive to dose than	
						temperature	

Table 2.3 continued

Alloy	Oxides	Test Reactor	Flux (n/m ² s)	Temp. (°C)	Dose (dpa)	Key Observations	Ref.
F94 ⁵	Y-Ti-rich	JOYO	—	400	2.5	No significant change to	[147]
F95 ¹	complex oxides			450	14	the chemistry or	
M93 ⁶				500	15	distribution of the oxides	
				330	7		
MA957	Ti oxides;	JOYO	—	502	101	Density of oxides 0.5 times	[11]
	Y-Ti-rich			709	100.5	lower but no significant	
	complex oxides					change in mean size	
MA957	Y-Ti-rich	HFIR	$2 - 5 \times 10^{18}$	600	3	No significant change to	[134]
	clusters					the chemistry or	
						distribution of the oxides	
ODS	Y-V-N-rich	BOR-60	1.8×10^{19}	330	32	Decrease in V and N but	[148]
EUROFER97	clusters					an increase in Cr and Mn	
						in oxides, dissolution of	
						large (≥ 10 nm) yttria	
						particles likely	

Table 2.3 continued

Alloy	Oxides	Test Reactor	Flux (n/m ² s)	Temp. (°C)	Dose (dpa)	Key Observations	Ref.
9Cr ODS ⁷	Y-Ti-rich clusters	ATR	9.7×10^{17}	500	3	No significant change to the chemistry or distribution of the oxides	[149]
MA957	Y ₂ Ti ₂ O ₇ ; Y-Ti-rich clusters	Phénix	—	412 430	50 75	At 430 °C, 75 dpa: some disappearance of oxides less than 2 nm in diameter, and change of oxide shape from sphere to cuboid.	[150, 137]
MA957	Y-Ti-rich clusters; Y-Ti-Al-rich clusters	ATR	—	287 417 340 478 380 498	0.12 0.12 1.02 0.68 4.15 3.9	Dissolution of some large ($r_G > 2.5$ nm) oxides, but no significant change to the size distribution of smaller oxides. Loss of O and Ti in the smaller oxides.	[135]

Table 2.3 continued

Alloy	Oxides	Test Reactor	Flux (n/m ² s)	Temp. (°C)	Dose (dpa)	Key Observations	Ref.
MA956	Y-Al-rich particles	ATR	2×10^{18}	328	4.36	Reduction in oxide number density by a factor of 2, as well as a slight reduction in average size.	[140]
PM2000	YAlO ₃	HFIR	—	500	21	Complete amorphization of the oxides. Increase in Y/Al ratio. No significant change to size distribution. Precipitation of Cr-rich and Al-Ti-rich phases in the matrix.	[141]

Table 2.3 continued

Alloy	Oxides	Test Reactor	Flux (n/m ² s)	Temp. (°C)	Dose (dpa)	Key Observations	Ref.
MA957	Y-Ti-rich clusters	FFTF/MOTA	—	412	109	Decrease in oxide number	[136]
				550	113	density as irradiation	
				670	110	temperature increased. No change in chemistry. Mo, Ni, Si, C, and B enriched at grain boundaries. Cr-rich clusters at 412 °C	
9Cr ODS ⁷	Y-Ti-rich clusters	ATR	—	500	3	Decrease in number density and size of oxides. Increase in the Y:Ti ratio of oxides after irradiation.	[151]
14YWT	Y-Ti-rich clusters	BOR-60	1.7×10^{19}	360 – 370	7	No significant change to the chemistry or distribution of the oxides. α' precipitation.	[152]

Table 2.3 continued

Alloy	Oxides	Test Reactor	Flux (n/m ² s)	Temp. (°C)	Dose (dpa)	Key Observations	Ref.
MA957	—	Osiris	2×10^{18}	325	2 5.5	No significant change to the chemistry or distribution of the oxides. α' precipitation.	[133]
ODS EUROFER97	—	HFR (Petten)	—	300	1 3	No significant change to the chemistry or distribution of the oxides.	[153]
125YF ⁸	Y-Al-rich particles	HFIR	—	215 357 557	1.8	No significant change to the distribution of the oxides. α' precipitation at 357°C. Increase in the Y/Al ratios of the oxides after irradiation.	[154]
¹ 12Cr-0.3Ti-0.25Y ₂ O ₃ ² 13Cr-2Ti-0.05Al-0.5Y ₂ O ₃ ³ 11Cr-0.4Ti-0.63Y ₂ O ₃ ⁴ 13Cr-0.6Ti-0.34Y ₂ O ₃ ⁵ 12Cr-0.3Ti-0.24Y ₂ O ₃ ⁶ 9Cr-0.2Ti-0.35Y ₂ O ₃ ⁷ 9Cr-2W-0.22Ti-0.35Y ₂ O ₃ ⁸ 12Cr-5.6Al-0.19Y							

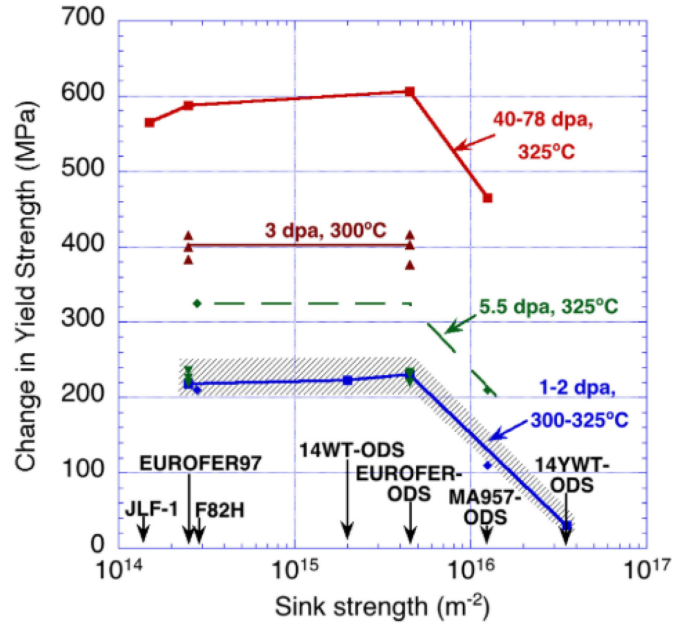


Figure 2.4: The effect of initial sink strength on LTBE for several RAFM and ODS alloys. Tensile tests were conducted at the same temperature as irradiation. Nanoclusters, grain boundaries, and network dislocations are included in the sink strength calculations. Reprinted from [6]

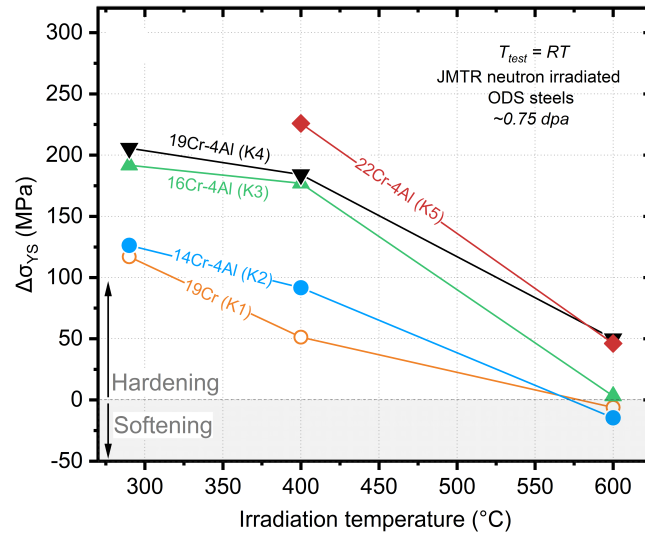


Figure 2.5: Increase in yield strength measured for several Fe-Cr and Fe-Cr-Al ODS alloys that were irradiated in Japan Material Test Reactor (JMTR) to ~ 0.75 dpa. Reprinted from [7]

Because hardening increased with Cr content, the authors attributed their results to α' precipitation [143]. However, aluminum additions were also observed to increase hardening. Further microstructure investigation is required to understand the underlying cause of this hardening and whether other ODS alloys may be similarly affected. It should be noted that for the first wall/blanket structure, fracture toughness is considered the most important mechanical property. Yield strength (σ_{YS}) and, by extension, hardness tends to correlate to fracture toughness, with harder materials demonstrating poorer fracture toughness. Thus, irradiation hardening at high temperatures is concerning as it may affect the lower operating temperature envisioned for fusion structures.

Another mechanical issue ODS alloys experience after irradiation is loss of tensile ductility. The capacity for uniform elongation can vary widely for irradiated ODS alloys based on composition. RAFM steels usually lose their capacity to uniformly elongate at low doses ($< 1\text{--}2$ dpa). However, some irradiated ODS alloys like MA957 appear to lose their capacity more gradually [7]. Nonetheless, after high doses (~ 40 dpa), the uniform elongation of ODS and RAFM steels both reach a comparably poor level ($< 1\%$). A problem specific to ODS alloys is loss of necking ductility. Even in the non-irradiated state, ODS alloys have much worse reduction in area ($< 50\%$) compared to RAFM steels ($> 80\%$) [7]. Additional data on the necking ductility of ODS alloys is therefore needed to understand its degradation after neutron irradiation. Such information would be valuable because literature suggests that in Fe-Cr steels, upper shelf energy scales with reduction in area, and so fracture toughness can be indirectly evaluated [155].

2.4 Summary and open questions

2.4.1 Factors affecting ballistic dissolution susceptibility

The recovery of different solute clusters to ballistic damage is usually assumed to be kinetically limited. However, such an assumption may be flawed since the change in solute concentration due to radiation enhanced diffusion depends not only on mobility, but also on thermodynamics (see Equation 2.14). Based on Fick’s second law of diffusion, the thermodynamic driving force for change in solute concentration is provided by the divergence of the solute concentration gradient. Interestingly, the Heinig precipitate stability model predicts that the solute concentration profile may be altered under irradiation [43]. Thus, what remains unclear is the relative importance of thermodynamics compared to kinetics, and whether modifications to the solute concentration profile under irradiation significantly affect the ballistic dissolution susceptibility of a cluster.

2.4.2 Contribution of phase instabilities to hardening in ODS alloys

It has been proposed that the high initial sink strength of ODS alloys should help to suppress low temperature hardening and embrittlement (LTHE) (see Figure 2.4). However, the data supporting this assertion is sparse and contradicting results exist [7]. Given that the lower operating temperature of the fusion first-wall/blanket structure is currently limited by LTHE, it is important to establish whether ODS alloys have similar embrittlement behavior to RAFM steels, for which hardness recovery typically occurs above 400 °C. In particular, a concern for high Cr ODS alloys compared to RAFM steels is α' precipitation. It is therefore important to understand the microstructure features responsible for LTHE in ODS alloys, and to quantify the contribution of solute nanoclusters formed due to phase instabilities.

2.4.3 Stability of oxides after high dose neutron irradiation

The expected damage levels for lead bismuth-cooled fast reactors, sodium-cooled fast reactors, and fusion power reactors are $\sim 50 - 130$, $90 - 160$, and $150 - 200$ dpa, respectively (see Figure 1.1). Despite these envisioned doses, there are few high dose neutron-irradiation studies to establish the stability of oxides in ODS alloys, which can be seen in Figure 2.6 where the studies in Table 2.3 are mapped according to temperature and dose. Further, the high dose studies that do exist tend to leverage only one characterization technique, such that a comprehensive assessment of phase stability including sink strength, structure, and chemistry is lacking. Thus, a goal of this thesis is to understand the full evolution of oxides particles with neutron irradiation dose.

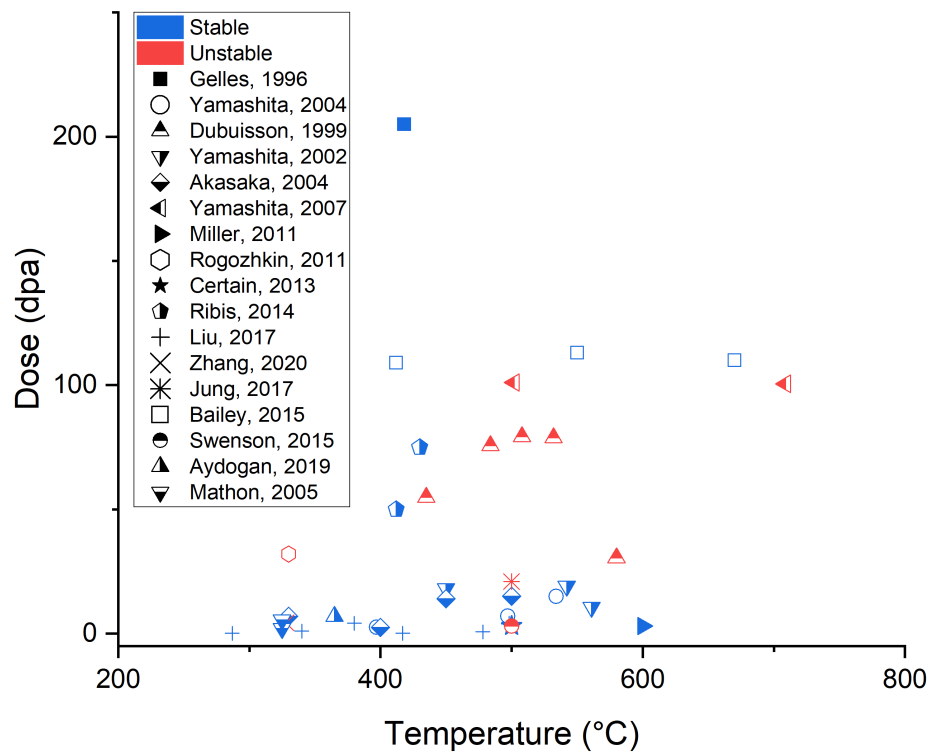


Figure 2.6: A map showing the temperature and dose for neutron-irradiation studies in ODS alloys. Blue symbols indicate the oxides were deemed stable, while red symbols indicate the oxides were considered unstable.

Chapter 3

Materials & Methods

3.1 Materials

3.1.1 304L austenitic stainless steel

The first class of structural materials to be examined in this study is austenitic stainless steel (AuSS). AuSS was selected because it is widely used for LWR core internals. Therefore, as demonstrated in Section 2, there is a vast amount of literature exploring radiation effects and in particular phase instabilities under irradiation in AuSS, covering a wide range of temperatures, dose rates, and doses. We would like to investigate the influence of ballistic effects on different cluster species in the same material for the same irradiation conditions to better understand factors important towards phase stability.

The specific material selected for this study was a solution annealed type 304L AuSS that was initially fabricated for a boiling water reactor core shroud (identified as Heat AS in Ref. [8]). It was neutron irradiated as part of the international Cooperative Irradiation-Assisted Stress Corrosion Cracking Program (CIR II) in the Boris 6 and 7 experiments. The chemical composition of the alloy is provided in Table 3.1.

Table 3.1: Chemical composition of 304L AuSS

	Fe	Cr	Ni	C	Si	Mn	P	S	Mo	N	Nb	Ti	O	Co	Cu
wt.%	bal.	19.95	10.80	0.023	0.56	1.82	0.023	0.015	0.53	0.072	<0.001	0.02	0.011	0.22	0.29
at.%	bal.	21.08	10.11	0.11	1.10	1.82	0.04	0.03	0.30	0.28	<0.001	0.02	0.04	0.21	0.25

Edwards et al. previously characterized the non-irradiated microstructure of this material by transmission electron microscopy (TEM) with a JEOL 2010F field emission gun (FEG) [156]. As this material is solution annealed, it contains a low initial dislocation density. High angle grain boundaries were enriched with P and slightly with Cr and Mo. Very few inclusions and no precipitates were detected in the microstructure prior to irradiation.

3.1.2 ODS steels

In addition to 304L AuSS, three varieties of ODS steels were selected for this study: PM2000, MA957, and 12YWT. The 12YWT was used strictly for mechanical property testing. Unlike for AuSS, there is substantially less literature on neutron irradiated ODS alloys, especially at high doses. Nonetheless, these materials are of immense scientific interest as ODS alloys continue to be developed for fusion first wall/blanket and sodium fast reactor cladding applications. The ODS alloys included in this study were selected because of their availability after high dose (> 50 dpa) neutron irradiation in the High Flux Isotope Reactor (HFIR). We would like to understand how phase instabilities under irradiation in these materials contribute to hardening and embrittlement, as well as the high dose degradation of the nanodispersoids.

PM2000

PM2000 is a commercial FeCrAl ODS alloy developed by Plansee GmbH that is being explored as a cladding alternative for sodium fast reactors. While the addition of Al enhances the alloy's corrosion and oxidation resistance, it also generates long-lived radioactive nuclides and therefore, PM2000 is not currently being considered for fusion first wall/blanket structures. The chemical composition of PM2000 measured by plasma optical emission spectroscopy (ICP-OES) is provided in Table

3.2. Overall, the microstructure consists of relatively coarse Y-Al-O nanodispersoids averaging 20 – 30 nm in diameter at a density of $\sim 10^{21} \text{ m}^{-3}$ [141, 157, 158]. In addition, it has large millimeter sized grains that are columnar and aligned along the extrusion direction [158].

MA957

Although MA957 was originally developed in 1978 by the International Nickel Company (INCO) for liquid metal fast breeder reactor applications, it is no longer commercially available. The MA957 used in this study was provided by CEA, Saclay. Samples were cut from the longitudinal direction of a thick-walled tube (6.5 cm outer diameter $\times$ 0.9 cm thickness). The chemical composition of the MA957 measured by ICP-OES is provided in Table 3.3. This specific heat of MA957 (HBB0127) has been analyzed in several previous studies [159, 160, 161]. According to atom probe tomography (APT) studies by Miller et al., the material contains a high density ($\sim 2 \times 10^{24} \text{ m}^{-3}$) of fine nanodispersoids (with average Guinier radius of 1.2 nm) that are Y-Ti-O-rich clusters [159]. Grain are also sub-micrometer sized, and elongated along the extrusion direction. Thus, the MA957 has a much higher initial sink strength compared to PM2000 and is classified by some as a nanostructured ferritic alloy.

12YWT

12YWT was an ODS alloy designed by Kobe Steel Ltd. in Japan in the 1990s [162]. It contains additions of tungsten, which causes strengthen by solid solution hardening. The full composition for 12YWT as measured by ICP-OES is provided in Table 3.4. The non-irradiated microstructure contains a high dislocation density, around 10^{16} m^{-3} [162]. In addition, the concentration of Y-Ti-O rich clusters is roughly $1\text{--}2 \times 10^{23} \text{ m}^{-3}$ with an average diameter is 2.6 nm [162, 163]. Grain size and aspect ratio are estimated to be 0.4–2 μm and 10–15, respectively [163]. Thus,

Table 3.2: Chemical composition of PM2000

	Fe	Cr	Al	Cu	Mn	Mo	Ni	Si	Ti	Y	O
wt.%	bal.	18.94	5.55	0.02	0.06	0.02	0.03	0.04	0.46	0.53	0.23
at.%	bal.	18.86	10.65	0.02	0.06	0.01	0.03	0.07	0.50	0.31	0.74

Table 3.3: Chemical composition of MA957

	Fe	Cr	Al	Cu	Mn	Mo	Nb	Ni	Si	Ti	W	Y	O
wt.%	bal.	14.34	0.08	0.02	0.05	0.29	0.04	0.32	0.04	0.92	0.01	0.26	0.20
at.%	bal.	15.15	0.16	0.02	0.05	0.17	0.02	0.30	0.08	1.06	trace	0.16	0.69

Table 3.4: Chemical composition of 12YWT

	Fe	Cr	C	Mn	Si	Ni	Mo	V	Nb	Ti	Cu	W	N	Y¹	O
wt.%	bal.	12.15	0.05	0.20	0.09	0.26	0.02	0.01	0.01	0.35	0.02	2.63	0.06	0.17	0.17
at.%	bal.	13.06	0.23	0.20	0.18	0.25	0.01	0.01	0.01	0.41	0.02	0.80	0.23	0.11	0.59

¹ estimated

similar to MA957, 12YWT can be considered a nanostructured ferritic alloy with high initial sink strength.

3.2 Irradiation experiments

3.2.1 304L AuSS BOR-60 neutron irradiations

Samples of 304L AuSS were irradiated in the BOR-60 sodium cooled fast reactor, which is part of the Research Institute for Atomic Reactors (RIAR) located in Dimitrovgrad, Russia. The samples were cylindrical tensile bars 33 mm in length with a gauge section 12 mm long and 2 mm in diameter. Neutron irradiations were conducted as part of the international Cooperative Irradiation-Assisted Stress Corrosion Cracking Program (CIR II) during the BORIS 6 and 7 experiments. Complete information on the irradiations is available in Ref. [8], and salient details are summarized here.

The outer housing of the irradiation rig consisted of two 1 mm thick hexagonal tubes separated by a 2 mm region filled with argon gas. Inside the housing, there was a capsule consisting of seven 35.5 mm diameter baskets stacked around a 6 mm diameter tube. The entire assembly was composed of Cr18-Ni10-Ti1 AuSS. In the capsule, dosimeters were located in the central tube at the level of each basket. In addition, Mg-Zn alloy thermal monitors and dosimeters were included in the rig. Two thermocouples also monitored temperature at the top of the rig near the sodium outlet.

During irradiation, the rig was radially located in the fifth row of the core, usually in cell D23. The samples were located within capsule baskets 4 and 7. The bottom of basket 4 was at the core center plane, and the top of the basket was 36 mm above. Basket 7 was 108 – 166 mm above the core center plane. Nominal fast neutron flux at the core central plane was $\sim 1.8 \times 10^{19} \text{ n/m}^{-2}\text{s}$ ($E > 0.1 \text{ MeV}$) at full power

(55 MWt). For basket 7, the fast flux was $\sim 30\%$, lower compared to the flux at the core central plane. A flux profile measured with dosimetry during the BORIS 3 campaign is provided in Figure 3.1 for reference.

The BORIS 6 and 7 irradiation campaigns spanned from June 26, 2001 to May 23, 2004. A total of 14 cycles were completed, starting with cycle 73 and ending with cycle 78B. At the start of cycle 73, samples AS13 and AS14 were located in basket 7 and sample AS22 was located in basket 4. After cycle 73A, all samples were unloaded from basket 7. The total fast fluence for samples AS13 and AS14 was approximately $9.94 \times 10^{23} \text{ n/m}^2$. Other samples, including AS17, were loaded into basket 7 and irradiated until the conclusion of cycle 75A. Sample A17 received a total fast fluence of $\sim 1.82 \times 10^{24} \text{ n/m}^2$. The samples in basket 4 remained loaded for all 14 cycles. As a result, sample AS22 received a total fast fluence of $\sim 6.65 \times 10^{24} \text{ n/m}^2$. A full irradiation cycle history is provided in Appendix 7, Table 3.

The average temperature of the BORIS 6 and 7 irradiations was $318 \pm 10^\circ\text{C}$, which is estimated from the average temperature of the sodium coolant. The error indicates the maximum deviation observed between the inlet and outlet sodium temperatures. Thermal fuse monitors using a Mg-Zn alloy were included among the specimens. The Mg-Zn alloy has a fusion (eutectic) temperature of $343 \pm 3^\circ\text{C}$. After irradiation, these monitors were checked for melting by X-ray radiography. Given that no melting was detected, it was verified that during the course of the experiments, irradiation temperatures did not exceed 343°C .

Irradiation damage in dpa-NRT was calculated by the RIAR using the SPECTER code. Based on these calculations, for types 304 and 316 SS, a fluence of $10^{22} \text{ n/cm}^{-2}$ corresponds to $\approx 5.2 \text{ dpa}$ and so the nominal damage rate at full power at the core central plane was $9.4 \times 10^{-7} \text{ dpa/s}$. The dose conditions are summarized in Table 3.5.

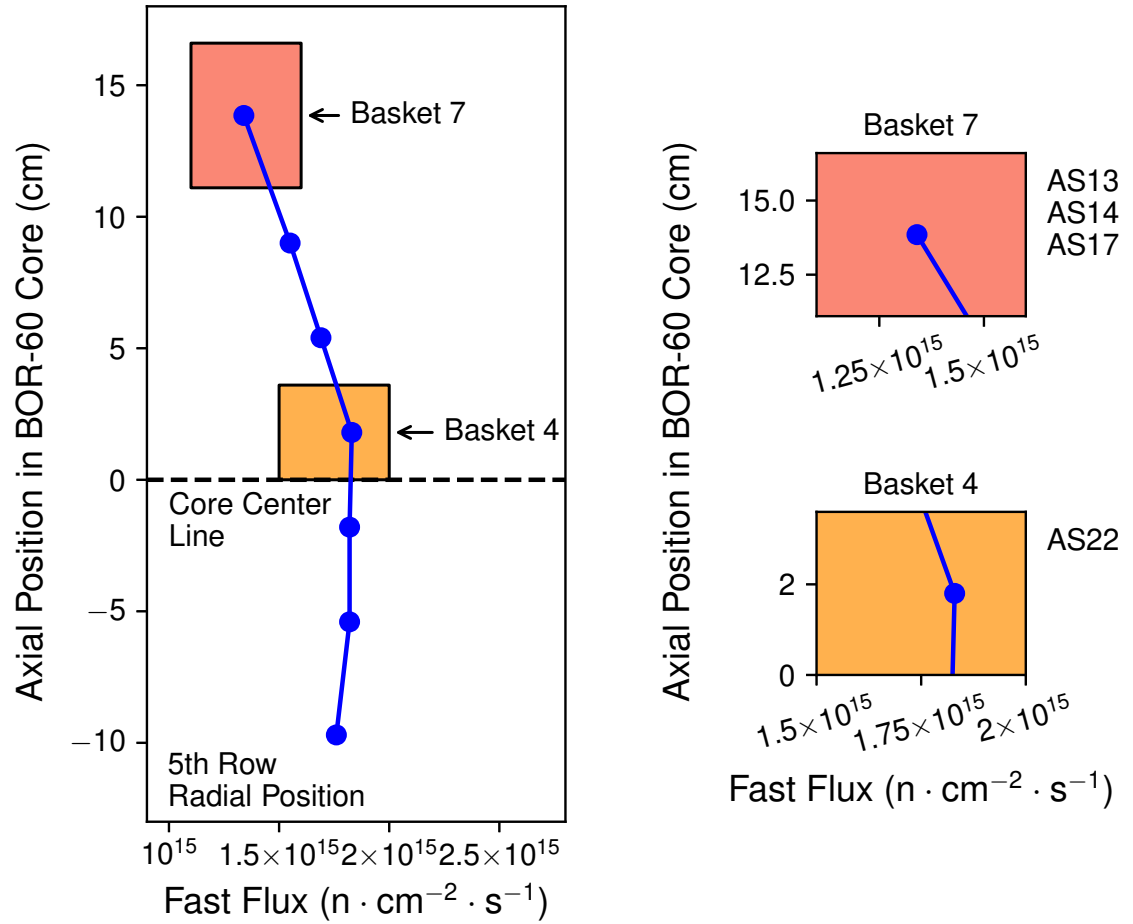


Figure 3.1: The fast flux ($E > 0.1$ MeV) profile of the BOR-60 core. Data from [8]. The vertical positions and flux profile across baskets 4 and 7 are shown.

Table 3.5: 304L AuSS neutron irradiation conditions included in this study. Irradiation temperature for all samples was $318 \pm 10^\circ\text{C}$.

Sample ID	Dose (dpa)
AS13	5.4
AS14	5.4
AS17	10.3
AS22	47.5

3.2.2 304L AuSS ion irradiations

Ion irradiations were conducted to add damage to 304L AuSS samples AS13 and AS14 that were initially irradiated in the BOR-60 reactor for 5.4 dpa. In preparation for the ion irradiation experiments, slices were cut from the grip sections of the tensile bars with a low speed diamond saw at the Low Activation Materials Development and Analysis (LAMDA) laboratory at Oak Ridge National Laboratory (ORNL). To minimize residual surface damage, samples were mechanically polished using SiC/diamond abrasives and then electropolished to a mirror finish.

Ion irradiations were conducted using a 3 MV Pelletron accelerator at the Michigan Ion Beam Laboratory. A defocused beam of 9 MeV Ni^{3+} ions was used to add up to 42 dpa (1.2×10^{17} ions/cm²) at 380, 400 and 420 °C at a damage rate of $\sim 1 \times 10^{-3}$ dpa/s to the 5.4 dpa BOR-60 samples. Because the damage rate of ion irradiations was higher than the BOR-60 fast neutron irradiations, an upwards temperature shift of at least 62 °C was used to keep the number of Frenkel defects lost to sinks invariant [164]. For 380 °C, the ion irradiation was divided into two separate experiments. In the first experiment, the ion dose was 4.7 dpa (1.3×10^{16} ions/cm²) and, in the second experiment, another 37.3 dpa (1.0×10^{17} ions/cm²) was added to the same sample (total = 42 dpa ion dose). At each irradiation temperature, the highest cumulative neutron plus ion dose was 47.4 dpa. Doses and temperatures for the ion irradiation conditions are summarized in Table 3.6.

To limit C contamination, samples and the chamber were plasma cleaned prior to irradiation for 2 hours, and a liquid nitrogen cooled cold trap was used during experiments. Vacuum chamber pressure was maintained below 10^{-7} torr. A cartridge heater and compressed air at the back of the irradiation stage were used to control temperature during irradiation. In addition, an infrared thermal imaging camera monitoring the sample surface and J-type thermocouples welded on

Table 3.6: Doses and temperatures for ion irradiation experiments on 304L AuSS.

Sample ID	Initial Condition	Ion Dose (dpa)	Ion Irrad. Temp. (°C)	Total neutron + ion dose (dpa)
AS13-1	AS13 (5.4 dpa BOR-60)	4.7	380	10.1
AS13-2	AS13-1 (5.4 dpa BOR-60 + 4.7 dpa ion)	37.3	380	47.4
AS14-1	AS14 (5.4 dpa BOR-60)	42	400	47.4
AS13-3	AS13 (5.4 dpa BOR-60)	42	420	47.4

neighboring samples were used to actively track sample temperature. The typical standard deviation for average sample temperatures was $\pm 5^\circ\text{C}$.

Damage and ion implantation profiles given in Fig. 3.2 were calculated with the Stopping and Range of Ions in Matter (SRIM-2013) program using the quick Kinchin-Pease method. A displacement energy of 40 eV was used for iron, chromium, and nickel. Damage was calculated using the VACANCY.txt output file. Doses reported are for an approximate mid-range depth of 1 – 1.4 μm , which was used for microstructure characterization.

3.2.3 ODS alloy HFIR neutron irradiations

PM2000, MA957, and 12YWT were irradiated in the 85 MW mixed-spectrum High Flux Isotope Reactor (HFIR) located at Oak Ridge National Laboratory as part of the JP-26, JP-27, and JP-29 campaigns. These irradiation campaigns were part of the JAEA-US DOE collaboration on fusion materials. All specimens were SS-J3 type flat tensile bars with dimensions 16 x 4 x 0.75 mm (length x width x thickness) and a gauge 5 x 1.2 mm (length x width). The SS-J3 tensile bars were loaded into capsules in a target rod assembly. Helium was used as a filler gas between the DISPAL[®] aluminum alloy capsule holders and the 6061-T6 target rod outer housing. The capsules were not instrumented, and so average temperature was verified after irradiation by dilatometry analysis of SiC passive temperature monitors.

Sample IDs are given in Table 3.7. The identifiers used for 12YWT, MA957, and PM2000 are ZP, ZQ, and ZR, respectively. The JP-26 irradiation campaign began on December 11, 2003 with cycle 398 and ended on November 10, 2004 with cycle 402b. The full irradiation cycle history is provided in Appendix 7, Table 1. Samples were exposed for 133.14 EFPD, during which the target rod was located in the C6 radial position of the HFIR flux trap. The fast flux profile annotated with

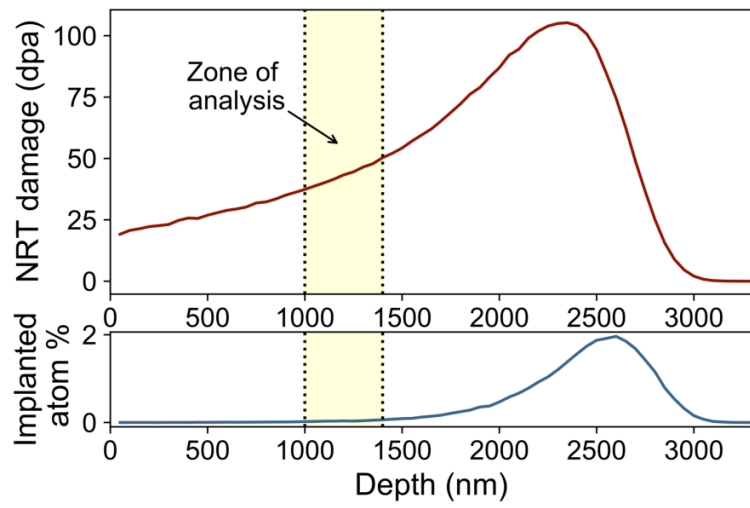


Figure 3.2: Implantation and damage profiles from SRIM for 9 MeV Ni^{3+} ion irradiations of 304L SS.

Table 3.7: ODS alloy neutron irradiation conditions included in this study. Samples used for mechanical testing and microstructure characterization are also indicated.

Sample ID	Base Material	Irrad. Temp. (°C)	Dose (dpa)	Mechanical Testing	Microstructure
ZP01	12YWT	335 ± 20	5.0	✓	—
ZP21	12YWT	500 ± 20	8.5	✓	—
ZP30	12YWT	335 ± 20	13.1	✓	—
ZP40	12YWT	450 ± 20	23.3	✓ ¹	—
ZP60	12YWT	279 ± 30	55.7	—	—
ZQ01	MA957	335 ± 20	5.1	✓	✓
ZQ10	MA957	450 ± 20	6.0	✓	✓
ZQ21	MA957	500 ± 20	8.6	✓	✓
ZQ30	MA957	335 ± 20	13.1	✓	—
ZQ41	MA957	450 ± 20	23.3	✓ ¹	—
ZQ60	MA957	287 ± 30	51.5	—	✓
ZR01	PM2000	335 ± 20	5.5	✓ ¹	✓
ZR10	PM2000	450 ± 20	6.5	✓ ¹	✓
ZR21	PM2000	500 ± 20	9.4	✓	✓
ZR60	PM2000	287 ± 30	55.9	—	✓

¹ Vickers microhardness only

the vertical positions of the relevant capsules is given in Figure 3.3. Samples ZP10, ZQ10, and ZR10 were in capsule 3a, which was located 20.7 cm above the reactor mid-plane. The fast neutron flux for this capsule was 7.31×10^{18} n/m²s and total fast fluence was 8.41×10^{25} n/m². Samples ZP21, ZQ21, and ZR21 were in capsule 11b, which was located 7.0 cm below the reactor mid-plane. The fast neutron flux for this capsule was 1.11×10^{19} n/m²s and total fast fluence was 1.28×10^{26} n/m². Finally, samples ZP01, ZQ01, and ZR01 were in capsule 16, which was located 22.7 cm below the reactor mid-plane. The fast neutron flux for this capsule was 6.46×10^{18} n/m²s and total fast fluence was 7.43×10^{25} n/m².

The design temperatures for capsules 3a, 11b, and 16 were 400, 500, and 300 °C, respectively. A limited number of SiC temperature monitors in the JP-26 target rod were analyzed after irradiation. Unfortunately, analyses of SiC monitors in capsules 3a, 11b, and 16 were not conducted. However, measurements of SiC temperature monitors in capsules 4, 5, 6, and 14 suggest that the average measured temperature was 335 °C for the 300 °C capsules and 450 °C for the 400 °C capsules [165]. No SiC thermometry data was available for the 500 °C capsules. An error of 20 °C is assumed for dilatometric analysis of the temperature monitors. The temperature of samples in capsules 3a, 11b, and 16 are therefore assumed to have similar error.

The JP-27 irradiation campaign began on April 27, 2004 with cycle 400 and ended on December 18, 2007 with cycle 412. Samples were exposed for 299.1474 EFPD. The target rod was located in the E2 radial position of the HFIR flux trap, which is an equivalent flux position to C6. Samples ZP30 and ZQ30 were in capsule 15b, which was 21.41982 cm below the reactor mid-plane, while samples ZP40 and ZQ41 were in capsule 5b, which was 9.82726 cm above the reactor mid-plane. The fast neutron flux for capsule 15b was 7.05×10^{18} n/m²s and total fast fluence was 7.96×10^{26} n/m². For capsule 5b, the fast neutron flux was 1.07×10^{19} n/m²s and total fast fluence was 1.82×10^{26} n/m². The target irradiation temperature was

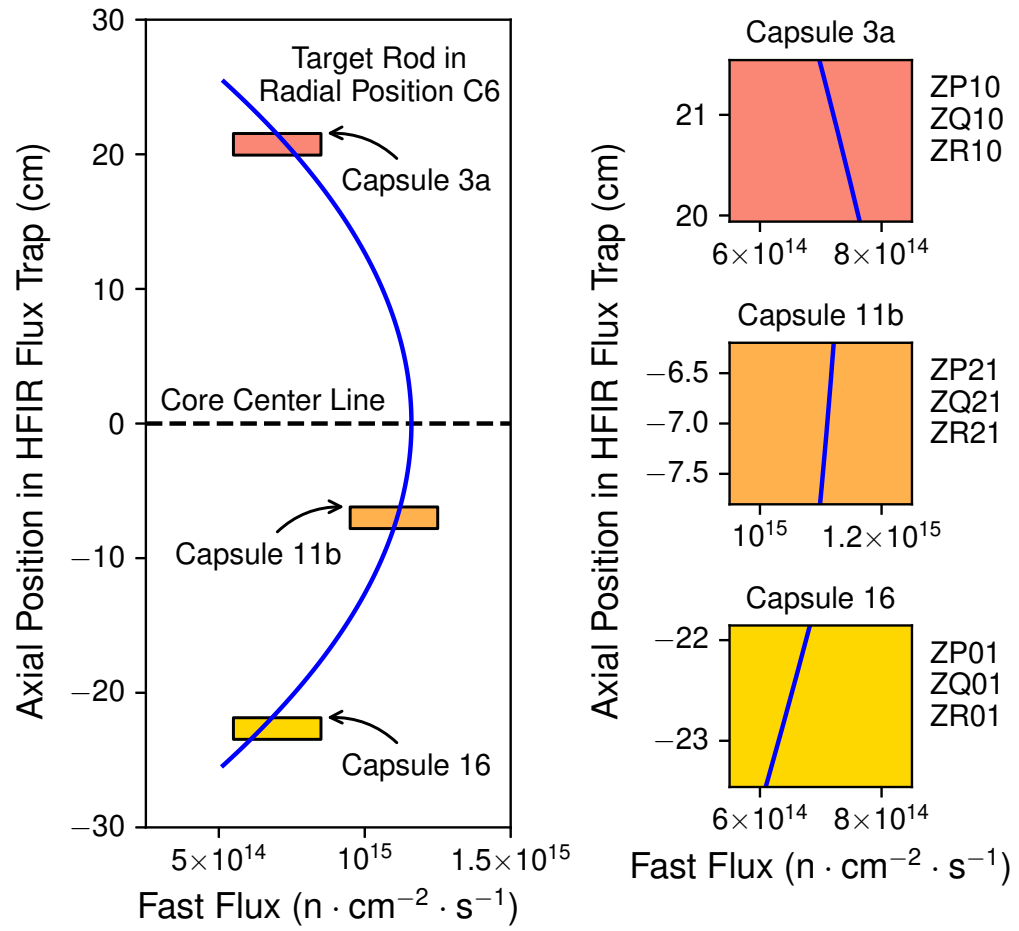


Figure 3.3: The fast flux ($E > 0.1$ MeV) profile for the target rod in the JP-26 irradiation campaign. The vertical positions and flux profile across capsules 3a, 11b, and 16 are shown.

300 °C for capsule 15b and 400 °C for capsule 5b. Similar irradiation temperatures to JP26 were measured.

The JP-29 irradiation campaign began on January 26, 2005 with cycle 403a and ended on July 13, 2013 with cycle 448. The full irradiation cycle history is provided in Appendix 7, Table 2. Samples were exposed for 1136.73 EFPD. The target rod was also located in the C6 radial position of the HFIR flux trap. The fast flux profile annotated with the vertical positions of relevant capsules is given in Figure 3.4. Sample ZP60 was in capsule 12b, which was 18.7 cm below the reactor mid-plane, while samples ZQ60 and ZR60 were in capsule 13a, which was 20.4 cm below the reactor mid-plane. The fast neutron flux for capsule 12b was $8.10 \times 10^{18} \text{ n/m}^2\text{s}$ and total fast fluence was $7.96 \times 10^{26} \text{ n/m}^2$. For capsule 13a, the fast neutron flux was $7.45 \times 10^{18} \text{ n/m}^2\text{s}$ and total fast fluence was $7.32 \times 10^{26} \text{ n/m}^2$. The target irradiation temperature for both capsules was 300 °C. In each capsule, two SiC monitors were measured. The actual temperature during irradiation for capsule 12 was $279 \pm 30 \text{ °C}$ and for capsule 13 was $287 \pm 30 \text{ °C}$.

For each sample, doses were calculated in dpa using FISTPACT-II. Details on the equations and atomic displacement energies are available in Ref. [142]. The dose and temperature conditions for each ODS sample are summarized in Table 3.7.

3.3 Microstructure characterization techniques

3.3.1 Atom probe tomography (APT)

Operating principles for APT

APT is a characterization technique that provides 3D chemical mapping information with a sub-nanometer spatial resolution. Just like field ion microscopy (FIM), from which APT originates, a high positive voltage (up to 15 kV) is applied

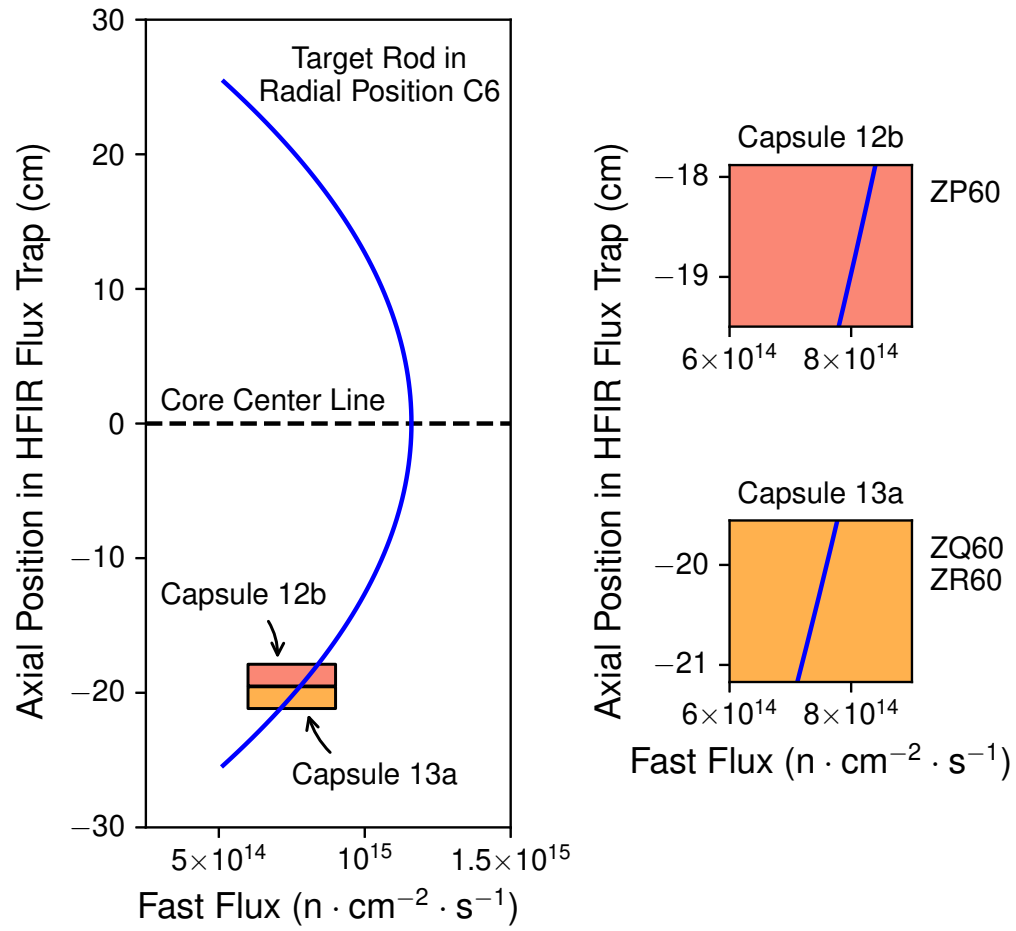


Figure 3.4: The fast flux ($E > 0.1$ MeV) profile for the target rod in the JP-29 irradiation campaign. The vertical positions and flux profile across capsules 12b and 13a are shown.

to needle-shaped specimens to generate a strong electric field. The electric field, F , can be calculated by:

$$F = \frac{V}{k_f R} \quad (3.1)$$

where V is the applied voltage, k_f is a constant known as the field factor that accounts for tip shape and the electrostatic environment, and R is the needle-shaped tip's radius of curvature.

To collect data in APT, the goal is for atoms near the specimen surface to be positively ionized and desorbed, a process known as field evaporation. While much is still unknown about the mechanisms involved with field evaporation, it is considered to be a thermally activated phenomena where surface atoms must overcome an energy barrier, Q . Thus, the number of atoms evaporated per unit time, which is evaporation rate, Φ_{evap} , can be described by an Arrhenius equation:

$$\Phi_{evap} = \nu \exp\left(-\frac{Q(F)}{k_B T}\right) \quad (3.2)$$

where ν is the atom vibrational frequency, k_B is Boltzmann's constant, and T is temperature. An applied electric field can reduce Q , and for a sufficiently high electric field, F_e , termed the evaporation field, the energy barrier will vanish. For metals, typical evaporation fields are around 10 – 60 V/nm [166].

Based on Equation 3.2, it is clear that field evaporation may be achieved either by increasing electric field or temperature. Thus, two modes of APT data acquisition exist: high voltage (HV) pulsing and laser pulsing. With HV pulsing, a negative voltage with an amplitude 10 – 25 % of the standing voltage, V_{DC} , is transmitted to a counter-electrode over a few nanoseconds. Ions are evaporated, and their charge may be multiplied during flight, as described by the post-ionization model [167]. Alternatively, with a picosecond or femtosecond pulsed laser, the apex of the

specimen. A key advantage of laser pulsing is that it can be used to promote the field evaporation of specimens with low electrical conductivity. In addition, laser pulsing may be more suitable for brittle materials, given that high electrostatic pressures (up to tens of GPa) from voltage pulsing can cause cyclic stresses, which can accelerate mechanical rupture of the specimen.

The field evaporation of a needle specimen is done in front of a position sensitive detector (PSD) so a projected image can be collected. Figure 3.5 shows a schematic of a typical atom probe setup. Commonly, a reverse-projection model is used to reconstruct atom positions from detector events. Using such a model, the magnification of the projection, M , can be estimated by:

$$M = \frac{L}{\xi R} \quad (3.3)$$

where L is the distance of the tip from the PSD and ξ is a constant known as the image compression factor (ICF). For finely sharpened APT needles less than 100 nm in radius, image magnification is on the order of 10^6 times [9]. It should be noted that an important assumption of the reverse-projection model is that the tip geometry is a perfect hemispherical cap on a truncated cone. However, the shape of the tip is likely to evolve as evaporation occurs. Voltage is usually monitored throughout experiments so that changes to the tip radius can be estimated with Equation 3.1. Alternatively, the tip radius can be predicted by assuming an initial geometry, and then estimating the contribution of each evaporated ion towards blunting the tip.

Unlike FIM, APT combines this projection imaging with time-of-flight spectrometry. The mass-to-charge ratio of an ion can be determined by relating its kinetic, $1/2mv^2$ where m is mass and v is velocity, and its potential energy, neV where n is the unit charge of the ion and e is the elementary charge of an electron. The standing electric field is used to accelerate evaporated ions towards the PSD. Modern atom probes usually have sufficient mass resolution to identify individual

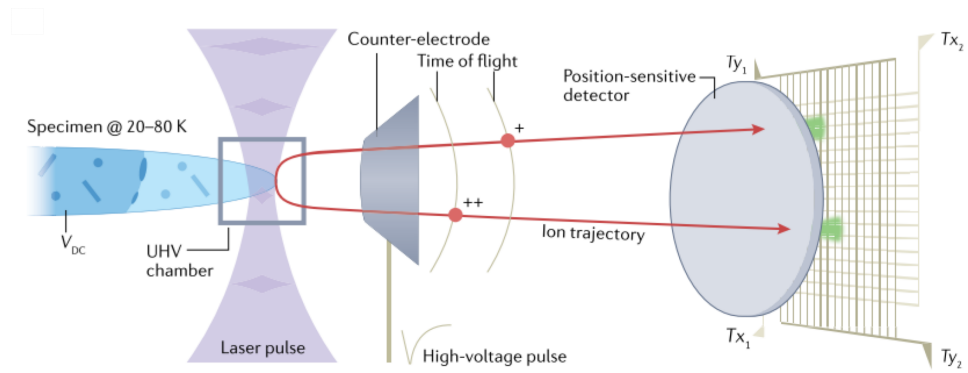


Figure 3.5: A schematic of an atom probe tomography system. Reprinted from [9].

isotopes. However, mass resolution can deteriorate if acquisition parameters are poorly selected. For instance, since most APT specimens have limited thermal conductivity, field evaporation can continue after a laser pulse has stopped. As a result, V_{DC} , wavelength, pulse duration, etc. all need to be carefully chosen to limit post-pulse evaporation, else these delayed events may broaden the tails of the mass peaks [168]. In general, one way to improve mass resolution for both pulsing modes is to increase the flight path so that time-of-flight is longer.

Possible APT artifacts

The needle in an APT system is similar to a lens in an optical system. Based on this analogy, anomalies that degrade the spatial resolution of reconstructions are often referred to as aberrations. Any deflection of an ion from its ideal flight path can be considered an aberration. One of the most common that occurs in APT is trajectory aberrations, which are caused by an uneven distribution of the electric field near the specimen surface [169]. The ramification of this is a lateral displacement of the ions at the beginning of their flight.

Local variations of the electric field may arise due to chemistry or crystallography. For example, trajectory aberrations are frequently observed for precipitates that have a different evaporation field compared to the matrix [170]. When the precipitate has an evaporation field lower than the matrix, the flight path of ions evaporated from the precipitate is compressed inwards. Thus, low-field precipitates constitute areas with high hit densities. The opposite relationship exists when the precipitate has an evaporation field higher than the matrix. In this case, because ion trajectories are deflected outwards, precipitate magnification in the x-y plane effectively increases, and a low-density zone can form around the precipitate. Table 3.8 contains the evaporation field for some ions relevant to this study.

Table 3.8: Evaporation fields for several ions of interest. Value are from [2].

Ion, i	Fe ²⁺	Cr ²⁺	Cu ⁺	Y ²⁺	Ti ²⁺	Ni ²⁺	Si ²⁺	Al ²⁺
Evaporation Field, F_e (V/nm)	33	29	30	24	26	36	33	35
Relative Field, F_e^i/F_e^{Fe}	1	0.88	0.91	0.73	0.79	1.09	1	1.06

In addition to degrading the spatial resolution, an important consequence of trajectory aberrations on precipitate analysis is that it may produce misleading compositional results. Matrix atoms are projected into a low-field precipitate when trajectories overlap. If the overlap is minor, only the composition at the interface may be affected [171]. However, for strongly overlapping trajectories, composition correction is required [172, 173].

Trajectory aberrations are also observed near crystallographic poles and zone lines. These are caused by terraces on the specimen surface, which exist due to the underlying structure, and locally increase the electric field [174]. Based on the higher than average local electric field, ions are deflected outwards. Thus, in materials where ions evaporate sequentially, low-index poles and zone lines can be observed on the desorption map as areas with low-hit densities.

The high electric field gradient near poles and zone lines can also produce surface migration artifacts, which in turn can cause erroneously high solute concentrations. Thermally assisted surface diffusion can be stimulated by the strong electric field gradients, initiating surface atoms to relocate to an adjacent position. Solute species with evaporation fields higher than the matrix tend to be more susceptible to surface migration since they are preferentially retained on the surface, and therefore have more time to diffuse. In ferritic alloys, the surface migration of Si, P, C, and Cr to low-index crystallographic poles have been reported [175, 176].

APT sample preparation

APT needles from bulk samples were milled by focused ion beam (FIB) using the FEI Quanta DualBeam and/or FEI Versa3D at the LAMDA laboratory. Initial lift-outs were made using 30 keV Ga ions. Material from these lift-outs were then welded to Si micro-tips. Sharpening of the tips were done with annular milling. The energy and current of the Ga beam were progressively reduced during the sharpening step to

avoid milling induced artifacts. For ion irradiated samples, needles were specifically milled to a depth 1 – 1.4 μm below the surface. Final tip polishing was performed using 2 keV Ga ions to remove near-surface regions damaged by the more energetic ions.

Data acquisition

For the 304L AuSS samples, all needles were run at the Michigan Center for Materials Characterization (MC²) using a Cameca LEAP 5000X HR except for the 5.4 dpa BOR-60 condition, which was run at the Center for Nanophase Materials Science (CNMS) at ORNL using a Cameca LEAP 4000X HR. For the ODS samples, all needles were run at CNMS on the LEAP 4000X HR. The ion detection efficiencies are 36 and 52 % for the LEAP 4000X HR and 5000X HR, respectively. Run parameters for each needle were kept consistent regardless of material or atom probe model. In all cases, data was collected in voltage mode at a temperature of 50 K, with a 20 % pulse fraction, a pulse rate of 200 kHz, and a detection rate of 0.2 – 0.5 %.

Mass-to-charge spectrum ranging

The peaks in the mass-to-charge spectrum were ranged to specific ions by selecting appropriate lower and upper limits. Each peak corresponds to a specific mass-to-charge ratio, m/z , given in units of Dalton (Da), equivalent to 1 atomic mass unit per coulomb. Although there is no standardized way to perform ranging, limits are typically set to start at the front edge of the peak and include a portion of the tail. Residual gases in the chamber can be ionized, and, as a result, peaks at 1, 2, 3, 17, 18, and 19 Da corresponding to H^+ , H_2^+ , H_3^+ , HO^+ , H_2O^+ , and H_3O^+ , respectively, are commonly appearing artifacts [166].

It is important to note that only one ion, either atomic or molecular, can be assigned to a single mass peak. This necessitates the deconvolution of isotopic peak overlaps. In the case of direct peak overlaps, two ions have the exact same m/z . Within the IVAS mass spectrum decomposition module, a corrected bulk composition is calculated based on:

$$f_{ij}A_i = \alpha_{ij}M_j \quad (3.4)$$

where f_{ij} is the isotopic abundance of ion i in range j , A_i is the actual total counts of ion i , α_{ij} is the fraction of ions in range j that are i , and M_j is the measured counts in range j [177]. Both A_i and α_{ij} are unknown, and by default in IVAS, f_{ij} is assumed to be the natural isotopic abundance. Equation 3.4 can be solved as an optimization problem, with the constraint that counts from all the peaks must be conserved before and after decomposition.

When there is nuclear transmutation, isotopic abundances may deviate substantially from natural abundances. In such cases, deconvolution must be performed outside of IVAS. To calculate the correct number of counts for each ion, a matrix equation can be used:

$$\mathbf{A}\vec{n} = \vec{r} \quad (3.5)$$

where $\mathbf{A}$ is the isotopic abundance matrix, $\vec{n}$ is the vector with the correct number of counts for each ion, and $\vec{r}$ is a vector with the counts from each ranged peak [178]. The isotopic abundance matrix has the shape $h \times i$ where h is the number of ranges and i is the number of ions. An example abundance matrix for the neutron irradiation of MA957 at 500°C to 8.6 dpa is provided in Appendix B, Table 6. Values for $\mathbf{A}$ are estimated by isotopic build-up calculations and $\vec{r}$ is known. Thus, $\vec{n}$ can be found by minimizing the squared residual of Equation 3.5.

For the AuSS specimens, ranging was done by hand, using visual inspection to select the lower and upper limits of each mass peak. A full list of ranges is provided in Appendix 7. Important isotopic overlaps in this material occur at:

- 27 Da: $^{54}\text{Cr}^{2+}/^{54}\text{Fe}^{2+}$
- 29 Da: $^{58}\text{Ni}^{2+}/^{58}\text{Fe}^{2+}$
- 31 Da: $^{62}\text{Ni}^{2+}/^{31}\text{P}^{+}$

Based on isotopic inventory calculations, transmutation products were considered to be negligible for the neutron irradiated AuSS specimens, and so natural isotopic abundances were used for decomposition of all datasets. The IVAS mass spectrum decomposition module was used to calculate a corrected bulk composition. Using this information, the concentration of element i in each solute cluster, X_c^i , was subsequently corrected by:

$$X_c^i = \frac{X_m^i B_c^i}{B_m^i} \quad (3.6)$$

where X_m^i is the measured composition of element i in the cluster, B_c^i is the corrected composition of element i in the bulk, and B_m^i is the measured composition of element i in the bulk before overlap correction.

To limit inconsistencies in mass spectrum analysis for the ODS alloys, ranging was done systematically by fitting an exponentially modified Gaussian function to each mass peak [179]. The limits for each range were selected to be full-width at nine tenths maximum (FW9/10M). An example is provided in Figure 3.6. A complete list of ranges for each ODS alloy are provided in Appendix 7. Some isotopic peak overlaps of note are:

- 14 Da: $^{14}\text{N}^{+}/^{28}\text{Si}^{2+}$

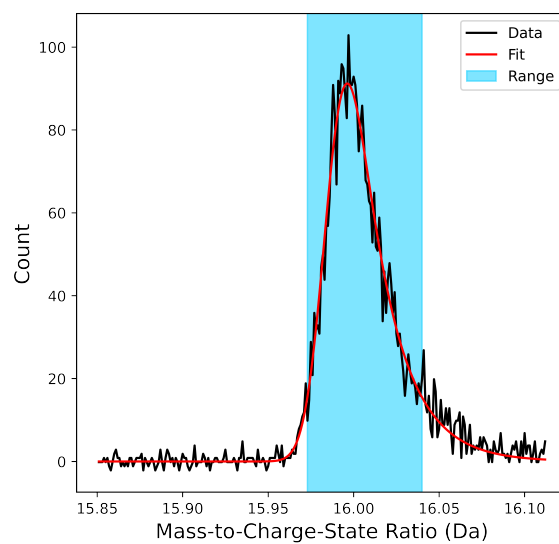


Figure 3.6: An example of the 16 Da peak in the mass-to-charge ratio spectrum, fitted with an exponentially modified Gaussian. Limits for the range are defined by the full-width at nine tenths maximum of the curve fit.

- 24 Da: $^{12}\text{C}_2^+ / ^{48}\text{Ti}^{2+}$
- 25 Da: $^{50}\text{Ti}^{2+} / ^{50}\text{Cr}^{2+} / ^{50}\text{V}^{2+}$
- 27 Da: $^{54}\text{Cr}^{2+} / ^{54}\text{Fe}^{2+} / ^{27}\text{Al}^+$
- 29 Da: $^{58}\text{Ni}^{2+} / ^{58}\text{Fe}^{2+}$
- 31 Da: $^{62}\text{Ni}^{2+} / ^{46}\text{Ti}^{16}\text{O}^{2+}$
- 32 Da: $^{16}\text{O}_2^+ / ^{48}\text{Ti}^{16}\text{O}^{2+} / ^{64}\text{Ni}^{2+} / ^{96}\text{Mo}^{3+}$

Isotopic inventories were calculated for each ODS sample and neutron irradiation condition with the FISTPACT-II code. These inventories were then used to form the isotopic abundance matrices that can be found in Appendix 7. The decomposed bulk composition of each APT volume was finally calculated by solving Equation 3.5 with the least squares method. To correct cluster compositions, Equation 3.6 was applied.

Needle reconstruction

Reconstruction of APT needles was performed with Cameca's Integrated Visualization and Analysis Software (IVAS), version 3.8.8. First, the lateral position of the atoms are determined. As discussed in Section 3.3.1, this is done using a reverse-projection model. Second, the depth coordinates for each atom is calculated. It is assumed that each ion evaporated from the surface causes an incremental change in the depth of the tip surface. Based on the identity assigned to each ion during mass spectrum ranging, there is an associated volume. When an ion is evaporated, the volume removed is spread across the surface of the tip so that the depth of the emitting surface increases accordingly. Assuming voltage is used to instantaneously determine the tip radius, the depth increment can be calculated by:

$$dz = \frac{\Omega L^2 k_f^2 F_e^2}{\eta S_D \xi^2 V^2} \quad (3.7)$$

where Ω is ionic volume, L is the length of the flight path, η is the detector efficiency, and S_D is the surface area of the detector [166].

Accurate volume reconstruction depends chiefly on the image compression factor ξ , the field factor k_f , the evaporation field F_e , and detection efficiency η . Since all the materials studied herein are Fe-based, F_e was assumed to be 33 V/nm, which is the evaporation field for Fe²⁺ [2]. For ODS alloy specimens, the values of ξ and k_f were calibrated based on the interplanar spacing, d_{hkl} , of crystallographic poles identified in the desorption map. In general, poles appear as areas with low hit density due to trajectory aberrations [174, 166]. The most common poles identified in the ODS samples were $\langle 110 \rangle$ and $\langle 200 \rangle$ with $d_{110} = 0.203$ nm and $d_{200} = 0.143$ nm. If two poles are identified, ξ can be calibrated based on the angle between the two poles. However, usually only one pole could be identified in the ODS samples, and so ξ was assumed to be 1.65. A value for k_f was determined by generating a spatial distribution map and changing the initial tip radius until the z-offset matched the expected interplanar spacing [180]. Unlike in the ODS alloys, no poles could be resolved in the AuSS specimens due to the high solute content of the alloy. A large quantity of solute atoms with different evaporation fields disrupts the sequence of field evaporation, and interferes with the imaging of atomic planes [174]. As a result, $\xi = 1.65$ and $k_f = 4.5$ was assumed for all AuSS reconstructions.

Cluster analysis

Solute clusters were identified with an iso-position algorithm written in Python called Open-Source Characterization of APT Reconstructions (OSCAR) [181, 182]. The basic steps for cluster identification are as follows. First, the local solute concentration within a fixed radius around each atom is calculated. Next, atoms

with a local solute concentration below a user defined threshold (c_{th} : **thres_conc**) are filtered out. The remaining atoms, which we shall call core atoms, are then formed into clusters based on a user defined linking distance (d_{link} : **dlink**). If the distance between two core atoms is less than or equal to the linking distance, those core atoms are merged into one cluster. After a cluster assignment is given to each core atom, clusters with less than a user defined number of solute atoms (N_{min} : **Nmin**) are excluded from further analysis.

To refine the size of each cluster, an erosion technique is used. As the width of the interface for each cluster may vary, a proximity histogram, concisely known as a proxigram, is first measured for each cluster. Proxigrams are generated by calculating the composition of each element in shells within and surrounding the cluster. A minimum of 25 atoms is required in each shell so that percent error does not exceed 20%. A four parameter logistic function is then fitted to the profile of a user-defined element. The erosion distance is taken as the absolute value of the logistic function x-midpoint (the x-value producing a response halfway between the minimum and maximum asymptote). A summary of the cluster parameters used in the analysis of each material is provided in Table 3.9.

The core composition of each cluster is simultaneously calculated in OSCAR when the proxigram is measured during cluster erosion. The core composition is recorded as the asymptote of the logistic curve fit for each element. The minimum asymptote is used if the slope factor of the logistic curve fit is positive, while the maximum asymptote is used if the slope factor is negative. If a logistic curve cannot be fit to an element's profile, the mean value of the profile is recorded as the element's core concentration.

OSCAR also includes a sphericity filter as a means to analyze cluster morphology. The filter calculates for each cluster a sphericity parameter, ψ , defined here as R_{eq}/R_G . R_{eq} is the equivalent spherical radius of a cluster given by equation 3.8

Table 3.9: Parameters used in the OSCAR program to identify solute clusters.

Base material	Solute(s)	Concentration threshold (c_{th})	Linking distance (d_{link})	Min. solute content (N_{min})
304L AuSS	Si	8.0	0.75	9
304L AuSS	Cu	5.0	1.07	8
PM2000	Cr	32.5	0.46	16
PM2000	Ti	5.0	1.16	8
MA957	Cr	30.0	0.49	16
MA957	TiO	3.5	1.02	6
MA957	Ni	6.0	0.72	6

where n is the number of atoms detected in the cluster, Ω is the atomic volume within the cluster, and Q is the detector efficiency.

$$R_{eq} = \sqrt[3]{\frac{3n\Omega}{4\pi Q}} \quad (3.8)$$

By contrast, a cluster's Guinier radius, R_G , is calculated with equation 3.9 based on the actual position of atoms within the cluster. Here m_j is the mass of atom j , r_j is the distance of atom j from the cluster's center of mass, and M is the total mass of the cluster.

$$R_G = \sqrt{\frac{5(m_1r_1^2 + m_2r_2^2 + \cdots m_jr_j^2)}{3M}} \quad (3.9)$$

A user defined tolerance (`tol`) determines the minimum value required to pass the sphericity filter. For the data herein, a tolerance of 0.25 was used and so the minimum passing value was 0.75. It should be noted that for a perfectly spherical cluster, ψ is expected to be unity.

The sphericity filter was specifically used to analyze Si-rich clusters in the AuSS. The goal of using the filter was to separate clusters nucleating homogeneously and forming due to RIS. Non-spherical clusters are expected to be RIS on dislocation lines and loops while clusters nucleating homogeneously are expected to be spherical, since this geometry minimizes the ratio of surface area to volume as described by critical nucleation theory. Equivalent spherical radius was calculated assuming a cluster atomic volume (Ω_{ppt} : `pptatvol`) of $1.2 \times 10^{-29} \text{ m}^3/\text{at}$, which is the atomic volume for G-phase ($\text{M}_6\text{Ni}_{16}\text{Si}_7$ with $\text{M} = \text{Ti, Nb, Mn, Fe and/or Cr}$).

Despite the improvements with OSCAR over the maximum separation method, there were still a few instances where clusters in close proximity were incorrectly linked together. This was evident either because the morphology of each cluster was noticeably different or because after erosion the clusters were disconnected.

As necessary, incorrectly linked clusters were separated using Ward’s minimum variance method [183]. The algorithm works by initially treating all atoms as singletons (clusters containing a single atom). Then, singletons/clusters are merged to minimize the variance of distance in each cluster. This is done recursively until the specified number of clusters is reached.

3.3.2 Scanning transmission electron microscopy (STEM)

As a complementary method to APT, many of the non-irradiated and irradiated specimens in this study were examined by STEM. Cross-sectional foils were fabricated from bulk materials at the LAMDA laboratory using the FEI Quanta DualBeam and/or FEI Versa3D FIBs. In most cases, samples were milled to a thickness of ~ 100 nm. Final polishing of the TEM foils was done with 2 keV Ga ions to limit surface damage. For the TEM foils made from MA957, samples were left slightly thicker than 100 nm and then flash polished. Flash polishing was performed with a solution of composed of 96% ethanol and 4% perchloric acid at -65°C with 41 V for 10 ms.

In STEM, an electron beam is converged by electromagnetic lens to form a probe that is then raster scanned across the foil. The signals generated from each point of the sample by the probe are collected by a series of detectors spanning various collection angles. The direct beam and signals scattered at very low angles with respect to the optic axis, around 0 to 10 mrad (smaller than the incident beam convergence angle), are collected by the bright field (BF) detector. These signals usually include Rutherford (elastic), phonon (thermal diffuse), plasmon, and Compton (inelastic) scattering. The detectors at intermediate collection angles, between around 10 and 50 mrad, are usually called low angle annular dark field (ADF) detectors. Finally, the detector spanning the highest collection angles, between around 50 to 150 mrad, is known as the high angle annular dark field

(HAADF) detector. The inner angle of the HAADF detector is significantly higher than typical angles of coherent Bragg scattering, and, therefore, the signal collected is primarily from incoherent Rutherford scattered electrons.

The microscope used for STEM and EDS spectrum imaging in this study was the FEI Talos F200X located in the LAMDA laboratory at ORNL. The operating voltage used for analysis was 200 kV. In addition, high resolution (HR) STEM work was performed at the CNMS at ORNL with the Nion UltraSTEM at an operating voltage of 200 kV. The Nion UltraSTEM is 5th order spherical aberration, C_s , corrected microscope. Spherical aberrations force rays passing at high angles to the optic axis to be focused at a point closer to the lens than rays passing at low angles to the optic axis, and so, without correction the high-angle rays produce smearing in the image. The point resolution limit of a TEM, quantified by $\sim C_s^{1/4} \lambda^{3/4}$, where λ is the electron wavelength, is therefore degraded by spherical aberrations. Spherical aberration correctors are multipole lenses capable of producing negative values of C_s that can be used to cancel out the positive C_s of round lenses. For the Nion UltraSTEM, 5th order aberration correction enables a HAADF spatial resolution of 0.8 Å at 200 kV under optimal conditions. Thus, atomic resolution imaging and analysis is possible.

Spectroscopy

When the incident electrons have an inelastic interaction with the sample, the resulting signals can be used for analytical TEM. If an electron imparts energy to ionize (eject) an inner-shell electron of an atom within the sample, the characteristic X-ray emitted when the atom relaxes can be leveraged for energy dispersive spectroscopy (EDS). With STEM, the X-ray signal at each point can be collected to produce a spectrum image. While powerful, EDS is a poor technique to quantify light ($Z \leq 10$) elements. Not only does X-ray fluorescence yield decrease

with atomic number, but also the energy of characteristic X-rays decreases with atomic number (Moseley's law). Thus, there is generally low detection efficiency for characteristic X-rays of light elements, since they tend to be absorbed by either the sample or other materials in the EDS system. As an alternative, electron energy loss spectroscopy (EELS), which is a technique that measures the energy of transmitted electrons after inelastic scattering with atoms in the sample, is better suited to quantify the composition of light elements. EELS has superior sensitivity for light elements compared to EDS because the number of transmitted electrons per inner-shell excitation and/or ionization is always one, regardless of atomic number, and the energy-loss electrons are scattered at low angles where they can be easily detected.

In addition to measuring elemental composition, EELS can also be used to analyze specimen thickness, valance/conduction electron density, dielectric properties, band structure, interband transitions, bonding, oxidation state, and distribution of near neighboring atoms. In this study, the thicknesses of TEM foils were measured with EELS. The zero-loss region of the EELS spectrum, spanning from approximately -2 to 5 eV, contains information from unscattered electrons, transmitted electrons without measurable energy loss, elastically scattered electrons, and quasi-elastically scattered electrons (produced by phonon scattering). By comparing the intensity of the zero-loss region, I_0 , with the intensity of the total spectrum, I_{tot} , foil thickness, t , can be calculated by the log-ratio method if the mean-free path for inelastic scattering, λ_{mfp} , is known:

$$t = -\lambda_{mfp} \ln \left(\frac{I_0}{I_{tot}} \right) \quad (3.10)$$

Contrast mechanisms

In this study, mass-thickness contrast was used for HRSTEM imaging or to distinguish between low and high atomic mass features, and diffraction contrast

was primarily used to image dislocation lines and loops. Mass-thickness contrast is the result of incoherent elastic scattering (Rutherford scattering). As previously mentioned, this type of signal is captured primarily by the HAADF detector in STEM. The differential cross-section for Rutherford scattering of an incident electron, $d\sigma_R(\theta)/d\Omega$, is:

$$\frac{d\sigma_R(\theta)}{d\Omega} = \left(\frac{Ze^2}{8\pi\epsilon_0 E_0} \right)^2 \frac{1}{\sin^4(\theta/2)} \quad (3.11)$$

where θ is the scattering angle, e is the elementary charge, Z is the atomic number of the target nucleus, ϵ_0 is the vacuum electric permittivity, E_0 is the initial kinetic energy of the bombarding electron, and Ω is the solid angle. As a result, the signal collected by a HAADF detector is roughly proportional to Z^2 . Given this relationship, it is common to refer to STEM-HAADF as “Z-contrast” imaging. For a TEM foil, the intensity of the Rutherford scattering signal, I_R , can be predicted based on the interaction cross-section by:

$$I_R = I_0 e^{-N\sigma_R t} \quad (3.12)$$

where I_0 is the intensity of the electron beam, N is the number density of scattering centers (electrons) in the sample, and t is the sample thickness. Thus, sample thickness also contributes to this type of contrast.

Another source of image contrast is the coherent elastic scattering of electrons, which results in Bragg diffraction. As the direct beam is collected by the BF detector and the diffracted beams are collected by the ADF detectors, the resulting images contain diffraction contrast. For the easiest interpretation and the strongest diffraction contrast, a two-beam condition, where the direct beam and only one diffracted beam are strong, is used. In STEM, to achieve a two-beam condition, the objective aperture must be used to select only one diffracted beam to limit

the collection of the ADF detector, or the diffraction pattern must be shifted, so the diffracted beam can be collected by the BF detector. Even with a two-beam condition, a challenge with using STEM compared to conventional TEM to produce diffraction contrast is that the incident beam is much less coherent due to its high angle of convergence. The coherency of the beam can be improved by using a small collection angle, but this leads to less signal and a more noisy image. Thus, for detailed analysis using diffraction contrast, conventional TEM is often preferred over STEM.

Strain from a defect produces an associated lattice distortion that can be imaged with diffraction contrast. For a perfect crystal oriented in a two-beam condition, the change in amplitude of the direct and the diffracted beam over a depth in the sample is described by the Howie-Whelan equations:

$$\frac{d\phi_0}{dz} = \frac{\pi i}{\xi_0} \phi_0 + \frac{\pi i}{\xi_g} \phi_g e^{2\pi i s_g z} \quad (3.13a)$$

$$\frac{d\phi_g}{dz} = \frac{\pi i}{\xi_0} \phi_g + \frac{\pi i}{\xi_g} \phi_0 e^{-2\pi i s_g z} \quad (3.13b)$$

where g is the diffraction vector of the Bragg reflection, ϕ_0 is the amplitude of the direct beam, ϕ_g is the amplitude of the diffracted beam, ξ_0 is the characteristic length (extinction distance) of the direct beam, ξ_g is the characteristic length (extinction distance) of reflection g , s_g is the excitation error (also known as the deviation parameter) for reflection g , and z is the distance within the specimen. The Howie-Whelan equations are modified if a lattice displacement R is introduced by a defect:

$$\frac{d\phi_0}{dz} = \frac{\pi i}{\xi_0} \phi_0 + \frac{\pi i}{\xi_g} \phi_g \exp [2\pi i (s_g z + g \cdot R)] \quad (3.14a)$$

$$\frac{d\phi_g}{dz} = \frac{\pi i}{\xi_0} \phi_g + \frac{\pi i}{\xi_g} \phi_0 \exp [-2\pi i (s_g z + g \cdot R)] \quad (3.14b)$$

As the intensity of the electron beam is proportional to the magnitude of its amplitude squared ($I \propto |\phi|^2$), the difference between equations 3.13a and 3.14a and between equations 3.13b and 3.14b can be used to explain the contrast produced by a defect during bright field and dark field imaging, respectively. It also becomes clear that when $g \cdot R = 0$, a defect will be “invisible” due to a lack of contrast. For dislocations with Burgers vector b , $R = b$ and therefore, the invisibility criterion is $g \cdot b = 0$. Thus, the diffraction condition must be well-known when performing dislocation analysis.

3.4 Mechanical testing

Post-irradiation mechanical testing of the neutron irradiated ODS samples was performed in the hot cells of the Irradiated Materials Examination and Testing (IMET) facility at ORNL. Vickers microhardness tests were performed at room temperature with a Mitutoyo HV-120B hardness tester in accordance with ASTM E384 (“Standard Test Method for Microindentation Hardness of Materials”). Indents were made on the grip-section of the SS-J3 tensile bars using a 1 kg load applied for a dwell time of 15 seconds. Per the ASTM standard, the distance between indents and the sample edge was greater than 2.5 dV, where the unit dV is the average Vickers diagonal distance. For good statistics, between 6 and 12 indent measurements were taken for each sample.

Uniaxial tensile tests were then performed at room temperature with the SS-J3 tensile bars in accordance with ASTM E8 (“Standard Test Methods for Tension Testing of Metallic Materials”). The samples were shoulder loaded and strained at a rate of 10^{-3} s^{-1} ($5 \times 10^{-3} \text{ mm/s}$ extension rate) using an Instron 5967 tensile frame. The 5 kN load cell of the frame was connected to a computer with Instron Bluehill3 analysis software. The tests were performed in air at room temperature.

Yield strength, uniform plastic elongation, and total plastic elongation were measured using the tangent modulus method based on the crosshead displacement because no gauge extensometer was included in the setup. Machine and load-train compliance effects can cause additional elongation in the pseudo-elastic regime, however neither the plastic regime nor calculated strength values are affected when measuring offset plastic deformation. Nonetheless, machine slack in the initial loading portion of the stress-strain curve was removed during data analysis.

The fracture surfaces of the SS-J3 samples were analyzed with a scanning electron microscope (SEM). Imaging was done using the secondary electron detector on a JEOL JSM-6010LA, which is a tungsten filament-based SEM. For each specimen, the reduction in area was quantified and general fractography was conducted.

Chapter 4

Factors affecting ballistic dissolution susceptibility

One challenge with using accelerated dose rate irradiations to predict reactor-relevant phase behavior is that high irradiation damage rates promote ballistic dissolution. Discussion on recovery to ballistic damage is often focused on how rapidly ejected solute atoms can diffuse back to their parent particle. However, solute fluxes require a concentration gradient. Given the ejection of solute atoms from the particle, the concentration profile near the particle interface is undoubtedly modified by irradiation. The question is to what degree does the recoil distribution modify the concentration gradient? In addition, do the irradiation conditions dictate the concentration gradient near the interface, or are there other relevant factors? To investigate these questions, the behavior of Cu- and Ni-Si-Mn-enriched clusters in a 304L austenitic stainless steel (see Chapter 3) was compared after high damage rate irradiation with ions and low damage rate irradiations in the BOR60 materials test reactor. **Note:** content in this chapter was published in *Materials & Design*, 217, S.M. Levine, C. Pareige, Z. Jiao, P.D. Edmondson, G.S. Was, S.J. Zinkle, A.

Bhattacharya, “Phase instabilities in austenitic steels during particle bombardment at high and low dose rates”, 110588, Copyright Elsevier (2022).

4.1 Results

4.1.1 Characterization of Cu-enriched clusters

Evolution under neutron irradiation

Cu atom maps sampled from each neutron irradiation condition and the corresponding clusters identified with OSCAR in each volume are shown in Fig. 4.1. At each dose, clustering of Cu atoms was observed. As shown in Fig. 4.2a, the number density of clusters increased from 5.4 to 10.3 dpa and then decreased at 47.5 dpa. Nonetheless, changes in number density were within an order of magnitude. Fig. 4.2b further shows that changes in average Guinier radius with dose were within experimental error. This implies neutron dose did not drastically coarsen the Cu-rich clusters. Cluster radius distributions at each dose, given in Fig. 4.3, were normal and symmetric. The standard deviation of size distributions at 5.4, 10.3, and 47.5 dpa was 0.32, 0.30, and 0.31 nm, respectively. Thus, the spread of the cluster size distribution remained relatively constant as well with increasing dose.

While the average sizes of the Cu-rich clusters did not change significantly with dose, Fig. 4.4 shows the average concentration of Cu in the cluster cores monotonically increased from 5.4 to 47.5 dpa. Even at 10.3 dpa compared to 5.4 dpa, cluster cores contained significantly more Cu (~ 15 at.% at 5.4 dpa and ~ 24 at.% at 10.3 dpa). Although Cu enriched more slowly in the cluster cores from 10.3 to 47.5 dpa, it is unclear without additional data at higher irradiation doses whether the clusters have reached their steady state composition. Besides Cu, these clusters were generally enriched in Ni and Si and depleted in Fe and Cr as compared to the matrix.

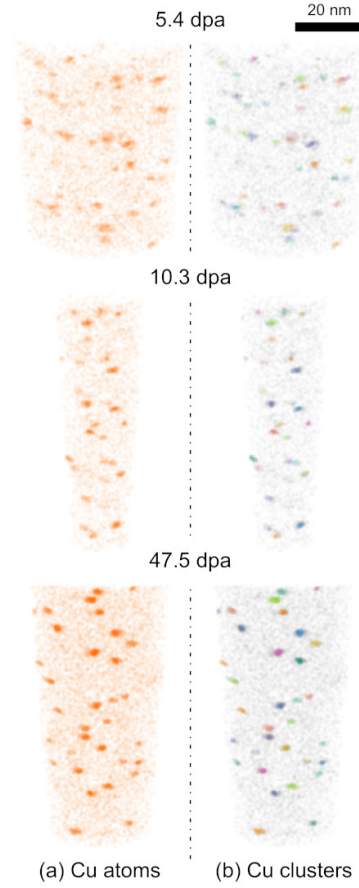


Figure 4.1: APT reconstructions showing Cu-rich clusters after fast neutron ($E > 0.1$ MeV) irradiations in BOR-60 at 318 °C. (a) Maps of Cu atoms and (b) the corresponding Cu clusters identified with OSCAR. Note that other elements in the clusters are not represented here. Neutron doses are shown above each reconstruction.

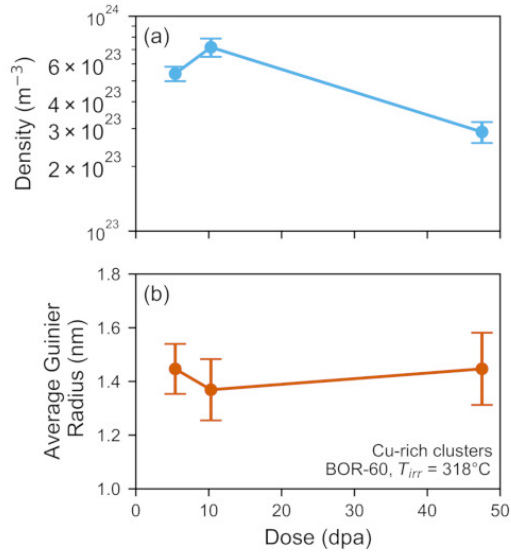


Figure 4.2: Evolution of the number density and average Guinier radius of Cu-rich clusters with BOR-60 neutron dose for irradiations at 318 °C. (a) Number density of Cu-rich clusters as a function of neutron irradiation dose and (b) average Guinier radius of Cu-rich clusters as a function of neutron irradiation dose.

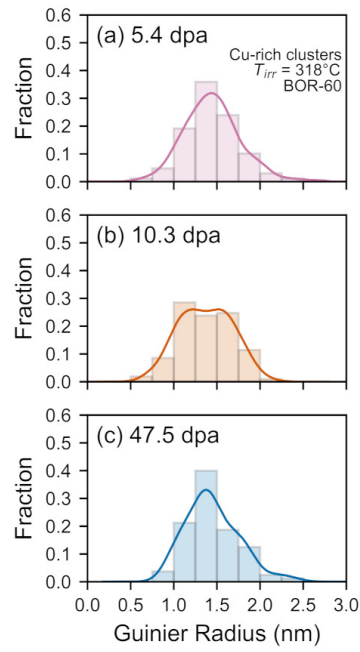


Figure 4.3: Size distribution of Cu-rich clusters for each BOR-60 neutron irradiation dose. (a) 5.4 dpa, (b) 10.3 dpa, (c) 47.5 dpa. Kernel density estimates are plotted as solid lines.

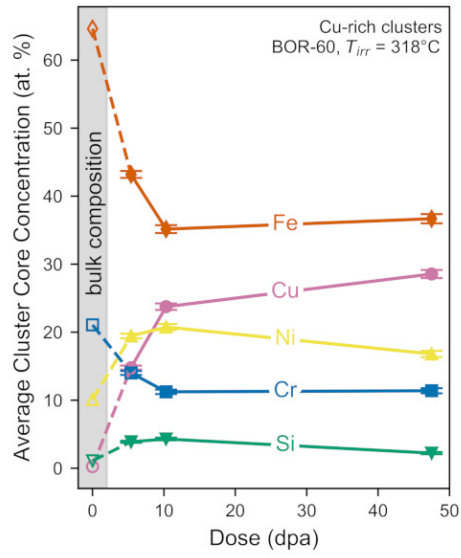


Figure 4.4: Evolution in average core composition of Cu-rich clusters with BOR-60 neutron irradiation dose. The initial bulk matrix composition is shown with open symbols in the gray shaded area for comparison.

Effect of ion irradiation on Cu-rich clusters formed during neutron irradiation

Cu atom maps from the 5.4 dpa BOR-60 samples that were self-ion irradiated and the corresponding clusters identified with OSCAR in those maps are given in Fig. 4.5. After the addition of 4.7 dpa by ion irradiation at 380 °C, Cu-rich clusters were present in low density. However, after the addition of 42 dpa by ion irradiation at 380 °C, resulting in a total neutron plus ion dose of 47.4 dpa, Cu-rich clusters had disappeared. Furthermore, Cu-rich clusters were also not detected in samples exposed to ion irradiation at the higher temperatures of 400 and 420 °C. Fig. 4.6a shows a comparison of evolution in Cu-rich cluster number density with dose for the neutron irradiated conditions and the combined neutron and ion irradiated conditions at 380 °C. The cluster number density dropped rapidly after an ion dose of 4.7 dpa and, as indicated by the dotted line, eventually falls to zero between an ion dose of 4.7 and 42 dpa. The evolution of average cluster size with dose is given in Fig. 4.6b for both the neutron irradiated conditions and the combined neutron and ion irradiated conditions at 380 °C. Even though the number density of Cu-rich clusters noticeably declined, the average Guinier radius of the remaining clusters did not vary significantly with 4.7 dpa ion irradiation. This suggests there was no inverse coarsening, and the pre-existing Cu-rich clusters were dissolved. Fig. 4.7 presents the average cluster core composition during the combined neutron and ion irradiations at 380 °C. Since no clusters were detected at an ion dose of 42 dpa, the alloy bulk composition is plotted at this dose for reference. The average cluster core composition barely regressed towards the bulk composition after 4.7 dpa ion dose. However, little change may be expected since ballistic dissolution occurs along the cluster interface, not in the core.

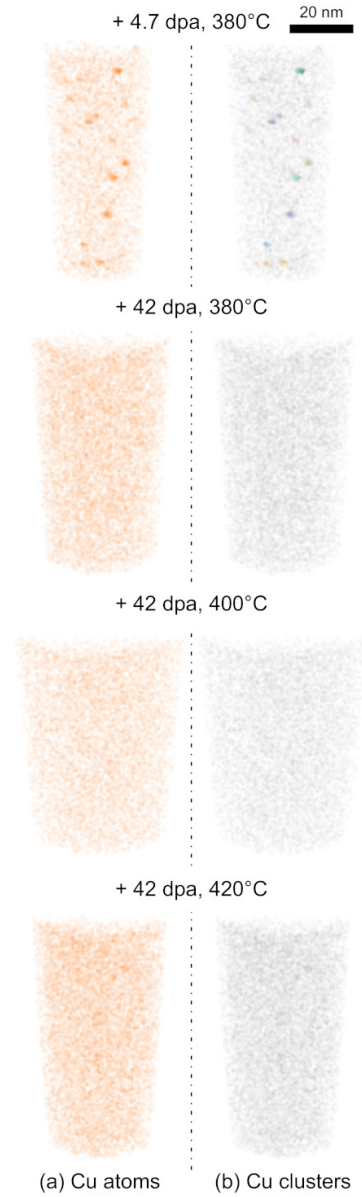


Figure 4.5: Evolution of Cu-rich clusters after ion irradiations on 5.4 dpa neutron irradiated samples. (a) Maps of Cu atoms and (b) the corresponding Cu clusters identified with OSCAR. Note that other elements in the clusters are not represented here. Samples were initially irradiated in the BOR-60 reactor for 5.4 dpa. Dose and temperatures overlaid here denote the conditions used for the ion irradiations.

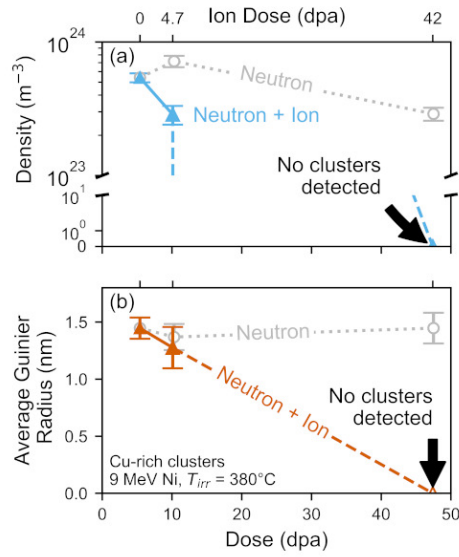


Figure 4.6: A comparison of the (a) number density and (b) average Guinier radius of Cu-rich clusters during neutron irradiation and combined neutron and ion irradiation at 380°C . Dashed lines are used to indicate that cluster number density and average Guinier radius for the combined neutron and ion irradiation are interpolated between an ion dose of 4.7 and 42 dpa as no clusters were detected at an ion dose of 42 dpa.

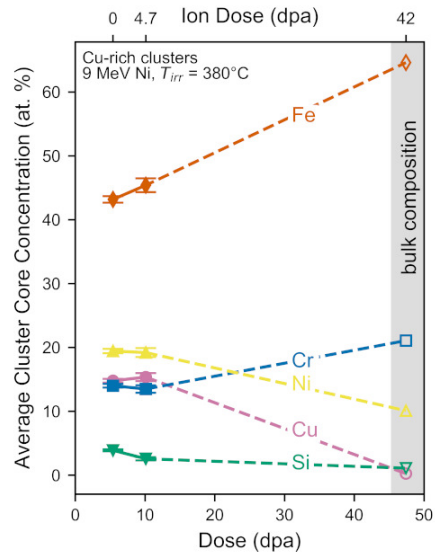


Figure 4.7: The evolution of Cu-rich cluster core composition with ion irradiation dose at 380°C. As no clusters were detected after an ion dose of 42 dpa, alloy bulk composition is plotted at this dose for reference. Dashed lines provide an interpolation of concentrations between an ion dose of 4.7 and 42 dpa.

4.1.2 Characterization of Ni-Si-Mn-enriched clusters

Evolution under neutron irradiation

Ni-Si- and Ni-Si-Mn-rich clusters formed after neutron irradiations. Since contrast between the Si concentration in the clusters and the matrix was the highest, we selected Si as the solute species to identify these clusters. Atom maps showing the distribution of Si and the corresponding clusters identified with OSCAR from each neutron irradiation condition are given in Fig. 4.8. Because Ni and Si can segregate to dislocation lines and loops in austenitic steels, we used the sphericity factor ψ to separate between clusters nucleating homogeneously and forming due to RIS. Unlike the Cu-rich clusters, numerous Ni-Si-rich clusters observed in the 5.4 and 10.3 dpa conditions were non-spherical ($\psi < 0.75$). Many of these features were linear, but some non-spherical features, such as the cluster shown in Fig. 4.9, were toroidal. These non-spherical clusters are expected to be RIS on dislocation lines and loops. In contrast with the low neutron doses, highly concentrated, large, spherical features were the dominant type of clusters observed at 47.5 dpa. We considered such Ni-Si-Mn-rich clusters with $\psi \geq 0.75$ to have formed by homogeneous nucleation (not by RIS to dislocation lines and loops).

For Ni-Si-Mn-rich clusters with $\psi \geq 0.75$, number density increased from 5.4 to 10.3 dpa but then decreased by 47.5 dpa, as can be seen in Fig. 4.10a. Overall changes in the number density were less than an order of magnitude. In Fig. 4.10b, the average Guinier radius for the Ni-Si-Mn-rich clusters at each dose is shown. Between 5.4 and 10.3 dpa, the average cluster size did not change significantly; however, by 47.5 dpa, the average Guinier radius of the clusters nearly doubled. Cluster radius distributions are given in Fig. 4.11. At 10.3 dpa, the size distribution was bi-modal, with the upper mode being more prominent. By 47.5 dpa, the distribution of Guinier radii returned to being uni-modal but shifted to higher values.

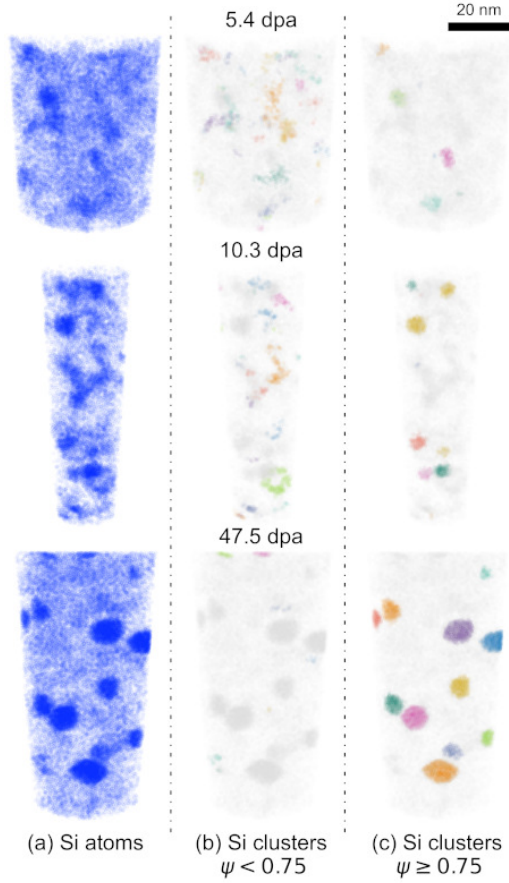


Figure 4.8: APT reconstructions showing Si-rich clusters after fast neutron ($E > 0.1$ MeV) irradiations in BOR-60 at 318 °C. (a) Maps of Si atoms. (b) and (c) are maps showing the corresponding Si clusters identified with OSCAR for $\psi < 0.75$ and $\psi \geq 0.75$, respectively. Note that other elements in the clusters are not represented here. Neutron doses are shown above each reconstruction.

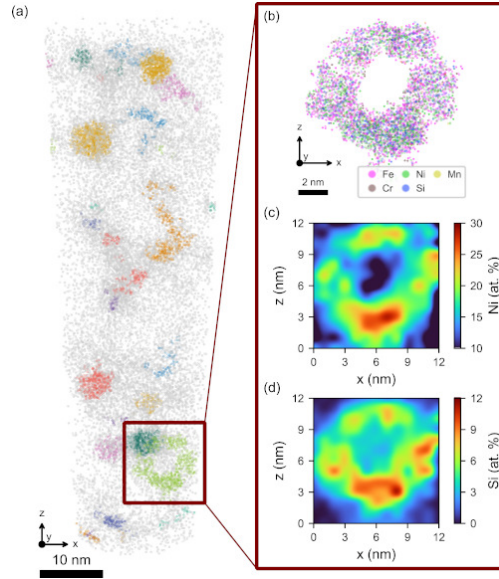


Figure 4.9: 3D reconstruction highlighting a toroidal cluster observed in an APT volume after BOR-60 fast neutron irradiation to 10.3 dpa at 318 °C. (a) Si atom map from the 10.3 dpa irradiation condition with all clusters highlighted, (b) a toroidal shaped cluster with all its constituent atoms, and (c) Ni and (d) Si 2D concentration profiles of the toroidal cluster. 2D concentration profiles were measured across a 12 x 12 nm area using a 6 nm thickness. No 2D concentration profile for Mn is provided, since Mn enrichment was not observed in this cluster.

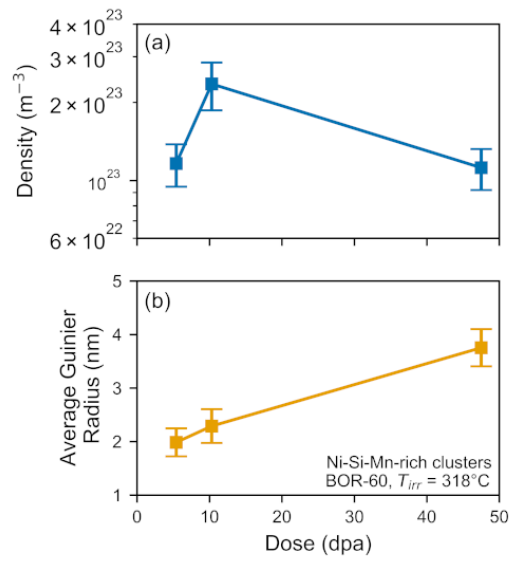


Figure 4.10: Evolution of the number density and average Guinier radius of Ni-Si-Mn rich clusters with BOR-60 neutron dose for irradiations at 318 °C. (a) Number density of Ni-Si-Mn-rich clusters as a function of neutron irradiation dose and (b) average Guinier radius of Ni-Si-Mn rich clusters as a function of neutron irradiation dose.

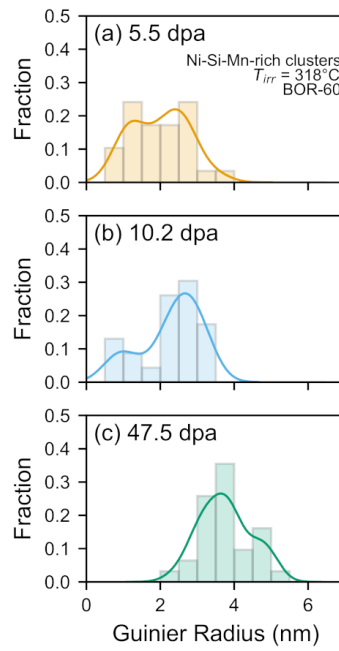


Figure 4.11: Size distribution of Ni-Si-Mn-rich clusters for after BOR-60 neutron irradiations at 318 °C. After (a) 5.4 dpa, (b) 10.3 dpa, and (c) 47.5 dpa.

In addition, the distribution appears to narrow slightly at 47.5 dpa as the standard deviation at 5.4, 10.3, and 47.5 dpa was 0.75, 0.79, and 0.68 nm, respectively.

The chemistry of the cluster cores as a function of irradiation dose is plotted in Fig. 4.12. Overall, Fe and Cr depleted from the clusters while Ni, Si, Mn, and P were enriched. By 5.4 dpa, the composition of the cluster cores had rapidly reached approximately 32Ni-17Si-3Mn-35Fe-9Cr-1P at.%. For all elements, cluster core concentration evolved monotonically with neutron irradiation dose. At 47.5 dpa, the average core composition was approximately 55Ni-22Si-11Mn-4Fe-3Cr-2P at.%, which closely resembles the composition of G-phase.

As noted previously, for the samples irradiated to 5.4 and 10.3 dpa, there were several non-spherical clusters observed ($\psi \leq 0.75$). These clusters had a unique core composition compared to the spherical clusters. In general, they contained less Ni, Si, Mn, and P and more Fe and Cr than the spherical clusters. For example, at 10.3 dpa the average core composition of the spherical clusters was approximately 41Ni-19Si-5Mn-23Fe-8Cr-2P at.% whereas it was approximately 25Ni-16Si-2Mn-40Fe-12Cr-1P at.% for the non-spherical clusters. Thus, these two species of clusters based on morphology and chemistry appear to be distinct, which supports the notion that Ni-Si-rich clusters may form by two different pathways: either due to RIS on dislocation lines and loops or by homogeneous nucleation.

Effect of ion irradiation on Ni-Si-Mn-rich clusters formed during neutron irradiation

The distribution of Si atoms in sample APT volumes after combined neutron and ion irradiation along with the clusters identified by OSCAR are given in Fig. 4.13. While Ni-Si-Mn-rich clustering was observed in each condition, clusters after adding 42 dpa ion dose at 400 and 420 °C appeared noticeably larger and well-defined compared to the clusters found in the samples ion irradiated at 380 °C. In

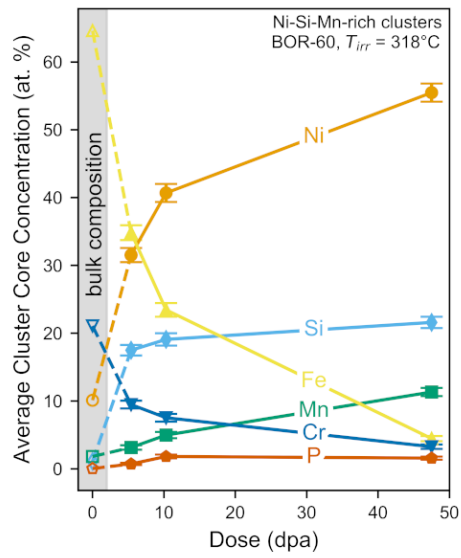


Figure 4.12: Evolution in average core composition of Ni-Si-Mn-rich clusters with BOR-60 irradiation dose. Initial bulk composition of the alloy is shown with open symbols.

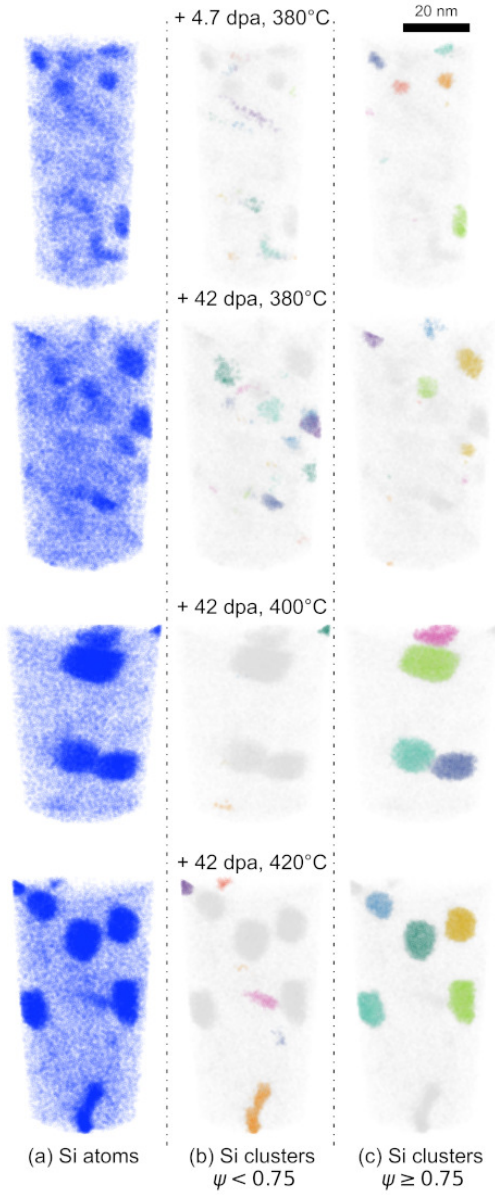


Figure 4.13: Evolution of Si-rich clusters after ion irradiations on 5.4 dpa neutron irradiated samples. (a) Maps of Si atoms. (b) and (c) are maps showing the corresponding Si clusters identified with OSCAR for $\psi < 0.75$ and $\psi \geq 0.75$, respectively. Note that other elements in the clusters are not represented here. Samples were initially irradiated in the BOR-60 reactor for 5.4 dpa. Dose and temperatures overlaid here denote the conditions used for the ion irradiations.

fact, several clusters in the samples ion irradiated at 380 °C were diffuse and non-spherical, similar to clusters in the 5.4 and 10.3 dpa BOR-60 conditions.

First, we present the results from combined neutron and ion irradiation at 380 °C. The evolution of Ni-Si-Mn-rich cluster number density with dose is given in Fig. 4.14a. Overall, cluster number density remained steady with increasing ion dose. Average cluster radius as shown in Fig. 4.14b also barely varied with ion irradiation dose at 380 °C. This contrasts with the increase in average Guinier radius observed with neutron irradiation dose, which is plotted as a dotted line in Fig. 4.14b for reference. A striking observation is the difference in cluster core compositions for the BOR-60 irradiated samples (Fig. 4.12) and the samples irradiated with both neutron and ions at 380 °C, shown in Fig. 4.15. As ion irradiation dose was increased from 4.7 to 42 dpa, only minor changes in cluster core composition occurred. The final composition of the clusters after an ion dose of 42 dpa was approximately 34Ni-18Si-2Mn-33Fe-10Cr-1P at.%. While Ni and Si were still enriched and Fe and Cr were still depleted in the clusters, the magnitude of these fluctuations after an ion dose of 42 dpa was noticeably lower than that observed after neutron irradiation. The average Ni, Si, and Mn core concentrations after 42 dpa ion irradiation were lower than those in the 47.5 dpa neutron irradiated clusters by ~ 39 , 15 , and 85% , respectively. After 42 dpa ion dose, the Mn concentration measured in the cluster cores was on par with the non-irradiated bulk concentration of Mn, indicating very little enrichment of Mn in the Ni-Si-rich clusters as compared to the neutron case. For the depleting solute species of Fe and Cr, differences between cluster core concentrations after 42 dpa ion irradiation compared to those after 47.5 dpa neutron irradiation were even more dramatic as they were higher by $\sim 647\%$ and 193% , respectively.

Ni-Si-Mn-rich clustering that developed during ion irradiation at 400 and 420 °C was appreciably different from the clustering observed during ion irradiation at 380 °C. As can be seen in Fig. 4.16a, for an ion dose of 42 dpa, cluster number

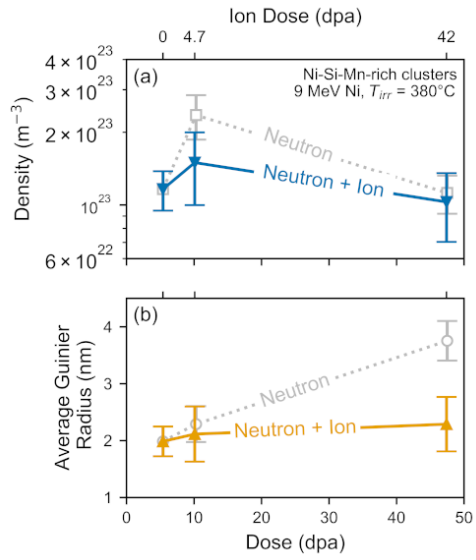


Figure 4.14: A comparison of the (a) number density and (b) average Guinier radius of Ni-Si-Mn-rich clusters during neutron irradiation and combined neutron and ion irradiation at 380 °C.

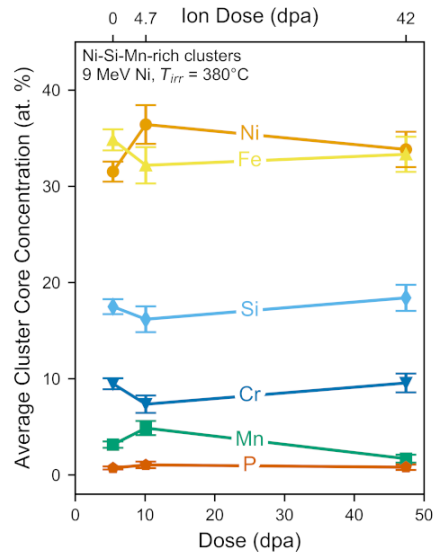


Figure 4.15: The evolution of Ni-Si-Mn-rich cluster core composition with ion irradiation dose at 380 °C.

density dropped by a factor of ~ 2 as ion irradiation temperature increased from 380 °C to 400 °C. This change was just within error, however, one must consider that percent error scales by $1/\sqrt{N}$, where N is the number of clusters counted, and, therefore, percent error is larger for the lower number densities. The difference in average Guinier radii when ion irradiation temperature was 400 or 420 °C compared to 380 °C was more pronounced. As shown in Fig. 4.16b, the average Guinier radius of the clusters was almost three times larger. In addition, the average Guinier radius of Ni-Si-Mn-rich clusters during combined neutron and ion irradiation to a total dose of 47.4 dpa (+ 42 dpa ion dose) at 400 or 420 °C was more than 1.5 times larger than the average Guinier radius of Ni-Si-Mn-rich clusters formed during neutron irradiation after a similar total dose.

Based on Fig. 4.17, where average cluster core composition is shown as a function of ion irradiation temperature for an ion dose of 42 dpa, it is clear that clusters formed after ion irradiation at 380 °C had a much lower Ni content compared to the clusters formed at higher ion irradiation temperatures. In fact, after ion irradiation at 400 and 420 °C, clusters cores had Ni and Si concentration values commensurate with G-phase. The average concentration of P in the cluster cores also increased with ion irradiation temperature, reaching ~ 4 at.% for the 420 °C condition. Finally, the average Mn concentration in the clusters after ion irradiation at 400 and 420 °C was only about 7.5 at.%, which is less than the approximately 11 at.% found within clusters formed during 47.5 dpa neutron irradiation. The composition of Ni-Si-Mn-rich clusters formed during combined neutron and ion irradiation was therefore slightly different from the composition observed for the same clusters formed during neutron irradiation.

It should be noted that a third type of Ni-Si-rich clustering feature was observed in the + 42 dpa condition at each ion irradiation temperature. These clusters had a platelet morphology as shown in Fig. 4.18. Unfortunately, these features were

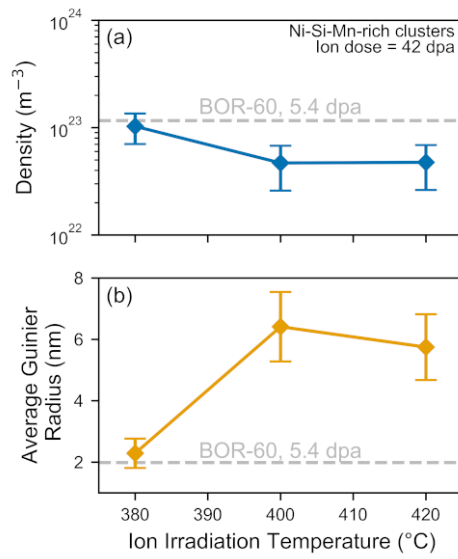


Figure 4.16: Influence of ion irradiation temperature on (a) number density and (b) average Guinier radius for Ni-Si-Mn-rich clusters at an ion dose of 42 dpa. The cluster density and average Guinier radius for BOR-60, 5.4 dpa, which was the starting condition for ion irradiation, are indicated by the dashed lines.

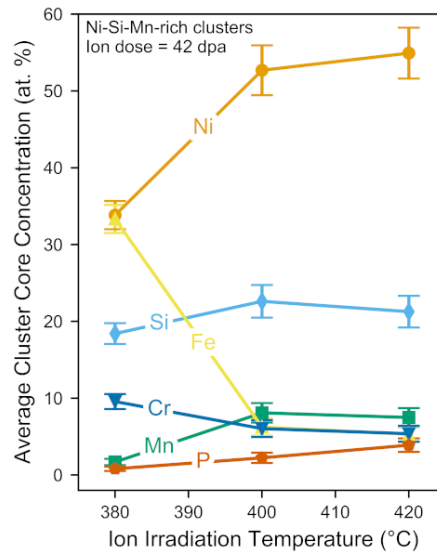


Figure 4.17: Average core composition of Ni-Si-Mn-rich clusters as a function of irradiation temperature for an ion dose of 42 dpa.

present in low number density and were often partially clipped at the edge of the APT tip volume, and so reliable quantitative information is difficult to provide. Qualitatively, the platelet shaped clusters were most prevalent and largest in the sample ion irradiated at 420 °C. The average composition of the platelet-shaped clusters in the 420 °C ion irradiated sample was 63Ni-27Si-0.4Mn-6Fe-1Cr-0.2P at.%. Thus, the Ni and Si content of these features was higher than in the spherical clusters. Manganese and phosphorus were noticeably absent from the platelet-shaped clusters as well.

4.2 Discussion

4.2.1 Radiation-enhanced formation of Cu-rich clusters during neutron irradiation

In this study, Cu-rich clusters appeared to nucleate and grow during neutron irradiation at 318 °C. Given the solubility of Cu in γ -Fe is approximately 0.009 wt.% at this temperature [184], the formation of Cu-rich clusters is likely to be radiation enhanced. It should be noted that the formation of Cu-rich clusters during neutron irradiation has only recently been reported [185]. Cu-rich clusters have also been observed after proton irradiation at 360 °C in commercial purity 304 [68, 186] and after self-ion irradiation at 380 °C in 304L [187]. Compared to proton and ion irradiations, neutron irradiations have lower damage rates and so ballistic mixing effects are reduced. In addition, the thermodynamic driving force for precipitation will be higher during neutron irradiation at 318 °C compared to the studies in Refs. [68, 186, 187], since supersaturation of Cu increases as temperature decreases. Thus, the stability of Cu-rich clusters during neutron irradiation is explicable.

The presence of Cu-rich clustering after self-ion irradiation in Ref. [187] contradicts our results where Cu-rich clusters were unstable under similar irradiation

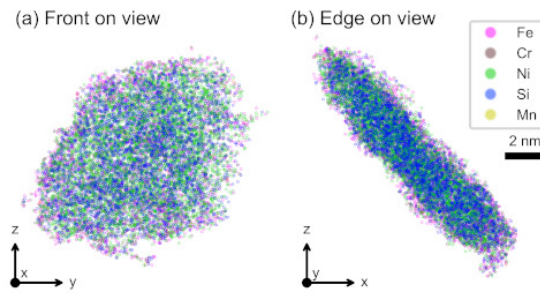


Figure 4.18: Example of Ni-Si-rich cluster with a platelet morphology from the + 42 dpa, 420 °C ion irradiation condition. (a) Front on view and (b) edge on view of the cluster. It should be noted that the cluster intersected the edge of the volume and therefore in the front on view the right-hand side of the cluster is slightly clipped.

conditions. This discrepancy may be due to differences in APT cluster analysis as the maximum separation method used to identify clusters in Ref. [187] is less stringent compared to the iso-position method used in this study. As a result, higher cluster densities are typically reported with the maximum separation method [188]. Another possibility is that injected interstitials may have suppressed clustering in our study. Recently, Lin et al. [189] revealed that for 8 MeV Ni ions implanted into pure Fe, the depth of the injected interstitial peak was overestimated with SRIM calculations by 38%. Assuming this SRIM calculation error is roughly the same for our experiments, the depth of examination in our study is much closer to the injected interstitial peak than in Ref. [187].

Even in an over-saturated solution with radiation enhanced diffusion, nucleation and growth of Cu-rich clusters appears to be slow. In this study, number density of Cu-rich clusters increased until 10.3 dpa, and the average amount of Cu in the cluster cores continued to increase up to 47.5 dpa. During proton irradiation of commercial purity 304 at 360 °C, the number density of Cu-rich cluster increased by an order of magnitude as dose increased from 5 to 10 dpa (with doses calculated using the full cascade option in SRIM) [68, 186]. All the aforementioned evidence suggests that Cu-rich clusters either develop late due to sluggish kinetics or nucleate non-classically [190].

Cu-rich clusters that formed during neutron irradiation by radiation enhanced precipitation were unstable during high damage rate ion irradiations between 380 and 420 °C. We presume the clusters do not completely dissolve in-cascade, since after 4.7 dpa ion irradiation at 380 °C there were still clusters observed. Rather, the gradual dissolution of Cu-rich clusters during ion irradiation likely occurs due to ballistic mixing. Given that the kinetics governing Cu-rich cluster nucleation and growth appear to be very slow, it is probable that radiation enhanced diffusion of Cu is not fast enough to counter the rate at which Cu is ballistically ejected from

the clusters. The effect of damage rate on Cu-rich cluster stability will be discussed further in section 4.2.3.

Aging experiments of austenitic stainless steels [191, 192] at 650 – 700 °C indicate that at thermal equilibrium, Cu precipitates are nearly pure Cu. However, following neutron irradiation the Cu-rich clusters observed in this study were noticeably dilute. Cu concentration in the cluster cores after 47.5 dpa was approximately 29 at.% while Fe concentration was approximately 37 at.%. In ferritic alloys, the Fe content of Cu-rich precipitates is a subject of open debate [193, 194, 195, 196, 197, 198]. Precipitates in Fe-Cu alloys are subject to local magnification effects when studied with APT [199]. However, there is evidence that trajectory aberrations in these alloys do not cause mixing in the precipitate core, and Cu-rich precipitates in fact contain some Fe [199, 200]. This hypothesis is also supported by thermodynamic studies [194, 196]. To determine the extent of trajectory aberrations in our experiments, atomic density relative to the bulk was measured in the x-direction across several clusters. An example profile is provided in Ref. [201]. Since Cu has a lower evaporation field (30 Vnm^{-1}) compared to Fe (33 Vnm^{-1}), a peak in the profile is expected if trajectory aberrations are significant; however, no peaks were detected. Without severe trajectory aberrations, matrix atoms should not overlap with the Cu-rich clusters. As a result, it is likely that in this study, the Cu-rich clusters actually do contain Fe. They may not have reached their equilibrium composition, or Fe from the matrix may have been ballistically injected into the clusters during irradiation.

Besides containing Fe, the Cu-rich clusters were also enriched in Ni and Si. The amount of Ni and Si in the clusters appeared to decline slightly after 10.3 dpa. Despite containing elevated amounts of Ni and Si, most of the Cu-rich clusters were homogeneously distributed. This aligns with the observation of Chen et al.

[186] where about one-third of the Cu-rich clusters were in contact with Ni-Si-rich clusters. In contrast, it was reported in Ref. [68] that most Cu-rich clusters were associated with Ni-Si-rich clusters. Given these contradictory results, the relationship between the Cu- and Ni-Si-rich clusters in irradiated austenitic stainless steels is still unclear. Analogous research in irradiated ferritic alloys shows Cu-rich precipitates are frequently surrounded by Mn-Ni-Si shells [202, 203, 204, 205]. It is believed that Ni and Mn segregation at the interface of Cu-rich clusters reduces the interfacial energy, thereby lowering the critical energy required for nucleation [206, 207, 208]. During the early stages of nucleation, Ni has also been detected in the core of Cu-rich clusters [209]. Jiao et al. [207] have suggested that another effect of Ni is it reduces the elastic strain energy associated with cluster nucleation. Further research is needed specifically on the kinetics and thermodynamics of Cu-rich cluster precipitation in austenitic stainless steels.

4.2.2 Classification of Ni-Si-rich clusters

In this study, three classes of Ni-Si-rich clusters were identified by comparing morphology and chemistry. The first class included linear and toroidal shaped clusters ($\psi < 0.75$) that appeared in the samples neutron irradiated to 5.4 – 10.3 dpa and the samples irradiated with neutrons and ions at 380 °C to a combined dose of 10.1 and 47.4 dpa. Because their shape resembled dislocation lines and loops, these clusters are expected to be due to RIS.

In general, dislocation cores are sinks for point defects, and self-interstitial atoms are attracted to the stress field surrounding dislocation cores. As a result, when solute atoms preferentially diffuse by an interstitial or vacancy mechanism, solute segregation can arise. In the case of austenitic stainless steels, the enrichment of Ni and Si at defect sinks (i.e. grain boundaries, dislocation lines, voids, etc.) is well documented [210, 66, 211]. Nickel predominantly enriches at sinks due to the

preferential diffusion of Cr over Ni by the inverse Kirkendall mechanism [212], while Si is known to arrive at sinks by an interstitial drag mechanism [213]. Toroidal shaped clusters abundant in Ni and Si have been observed in several other APT studies of irradiated austenitic stainless steels [68, 186, 70]. Further evidence that these clusters may result from RIS to dislocation cores is provided by Etienne et al. in Ref. [214], where the number density of Si-rich clusters observed by APT in ion irradiated cold worked 316SS was correlated to the density of dislocation loops observed by TEM.

The second class of Ni-Si-rich clusters observed included clusters that had a spherical morphology ($\psi \geq 0.75$). In most cases, these clusters were also rich in Mn. For the sample irradiated in BOR-60 to 47.5 dpa and the samples ion irradiated at 400 and 420 °C for 42 dpa, Ni and Si concentrations in the clusters were commensurate with G-phase and thus these clusters are expected to be G-phase precipitates. By extension, the spherical clusters observed at lower neutron doses and also at lower ion irradiation temperatures are believed to be G-phase embryos. Indeed, the Ni/Si ratios for the spherical clusters observed in the samples neutron irradiated to 5.4 and 10.3 dpa were 1.8 and 2.1, respectively, which approaches the Ni/Si ratio in G-phase (≈ 2.3).

Differences in the Mn and P content of G-phase formed during neutron irradiation and combined neutron and ion irradiation are likely related to RIS. Phosphorus is known to segregate to surfaces in austenitic stainless steels under thermal conditions [215] and its segregation is enhanced under irradiation through migration by interstitial binding [216, 68]. The mechanism by which Mn accumulates in G-phase precipitates is less clear, since Mn normally depletes at grain boundaries in austenitic alloys [217, 68]. However, recent first-principles calculations suggest that, due to magnetic effects, Mn can potentially bind with interstitials despite being an oversized solute [218]. Nevertheless, mystery still surrounds the role of

Mn in Ni-Si-rich cluster formation, which is also a topic of major debate for similar clusters in irradiated ferritic alloys [219, 220].

While G-phase is a well-known radiation induced phase in austenitic stainless steels, it is typically observed in 316 and not 304 stainless steel [73]. In addition, G-phase in 300-series stainless steels irradiated with neutrons at LWR-relevant temperatures is rarely reported. However, there is growing evidence that G-phase can precipitate in 304SS and at irradiation temperatures below 400 °C. Recently, Isobe et al. detected a fine distribution of G-phase in X18H9, which is analogous to AISI 304, irradiated in the BN-600 fast reactor at 370 – 375 °C [221]. Also, although the phase could not be definitively identified based on electron diffraction patterns, potential G-phase precipitation was suspected in Refs. [156, 222] for 304SS variants irradiated in BOR-60 at approximately 320 °C.

The last class of Ni-Si-rich clusters, observed only in the samples irradiated with both neutron and ions, included platelet shaped clusters ($\psi \leq 0.75$). While the average Ni to Si ratio for the platelet-shaped clusters was 2.3, these clusters had no Mn enrichment. In fact, the average Mn core concentration of these clusters was approximately 0.4 at.%, indicating Mn was depleted. In addition, the core Ni and Si content of these clusters exceeded values of stoichiometric G-phase (i.e. > 55 at.% for Ni and > 21 at.% for Si), reaching as high as 68 at.% Ni and 29 at.% Si. Given their composition, these platelet-shaped clusters are unlikely to be G-phase precursors. Although they had different chemistry compared to the present study, platelet-shaped features were also reported by Etienne et al. in neutron and ion irradiated cold-worked 316 stainless steel [223, 70]. While the nature of these features remains ambiguous, we hypothesize that the platelet shaped clusters are Frank dislocation loops where significant solute accumulation occurs, covering the entire habit plane. Besides at dislocation cores, Ni and Si enrichment on the habit plane of Frank loops has been observed in the past with analytical electron microscopy [224]. Since the

area bound by a Frank loop is a stacking fault, solute segregation on the habit plane may reduce stacking fault energy [225] and, by extension, loop energy. Consistent with this, molecular statics calculations for the Ni-Fe system have validated that due to the stress field induced by a stacking fault, the lowest energy configuration for solute segregation can be on the habit plane of a faulted dislocation loop [226].

There is some evidence that microstructure and irradiation conditions may affect the formation of the platelet-shaped clusters, since this type of cluster was not observed after neutron irradiation. The number density of spherical clusters suspected to be G-phase precipitates after 42 dpa ion irradiation was lower than after 47.5 dpa neutron irradiation. Thus, precipitates are expected to contribute less to the overall sink strength in the ion irradiated samples. With fewer sinks for point defects to partition to, RIS of Ni and Si to dislocation loops should be more pronounced. Assuming the platelet-shaped clusters are faulted dislocation loops with solute atoms accumulated on the habit plane, greater RIS at dislocation loops should promote the formation of these clusters.

4.2.3 Effect of damage rate on cluster stability

Both Cu- and Ni-Si-Mn-rich clusters were able to nucleate during neutron irradiation. However, subject to ion irradiation, Cu-rich clusters dissolved while Ni-Si-Mn-rich clusters were retained. This suggests that compared to the Ni-Si-Mn-rich clusters, the Cu-rich clusters have a greater susceptibility to ballistic dissolution and/or have a weaker ability to recover from ballistic attack. The most simplistic model that balances recoil dissolution and the diffusion of solute to precipitates is the Nelson, Hudson, Mazey (NHM) model [227]. However, the NHM model assumes recoil distances are infinitely large and therefore incorrectly represents the solute concentration gradients near the particle interface [228, 44]. As an improvement, the Heinig model [43] employs an exponential recoil distribution. A key concept

proposed by the Heinig model is that under irradiation, the capillary radius, r_{cap} , of precipitates can be modified. Under thermal conditions, r_{cap} is equal to $2\sigma V_m/R_g T$ where σ is interfacial energy, V_m is molar volume of atoms in the precipitate phase, R_g is the universal gas constant, and T is temperature. However, the effective capillary radius of a precipitate under irradiation, r_{cap}^{irr} , is given by:

$$r_{cap}^{irr} = \frac{4r_{cap} - 5\lambda\Delta}{4(1 + \Delta)} \quad (4.1)$$

where Δ is defined as:

$$\Delta = \frac{q\phi\lambda^2}{D^{irr}C_\infty} \quad (4.2)$$

Here λ is the mean displacement distance, q is the mixing rate, ϕ is the flux, D^{irr} is the irradiation enhanced diffusion coefficient of the solute species, and C_∞ is the equilibrium concentration of solute in the matrix near a particle of infinite radius. Precipitate stability is expected at a given dose rate for the critical temperature where $r_{cap}^{irr} = 0$. When r_{cap}^{irr} is positive, Ostwald coarsening of the precipitates occurs based on the Gibbs-Thomson effect. On the other hand, when r_{cap}^{irr} is negative, inverse coarsening of the precipitates is predicted. One shortcoming of the Heinig model is that it does not predict ballistic dissolution, only inverse coarsening. It is important to note though that if λ is below some critical relocation distance, R_c , inverse coarsening is precluded, and only ballistic dissolution can occur [44]. However, determining R_c requires computational modeling, which is beyond the scope of this paper. And so, the goal herein is to use the Heinig model to explain the experimentally observed results for Cu- and Ni-Si-Mn-rich clusters under neutron and ion irradiation. Specifically, for the clusters nucleated after 5.4 dpa neutron irradiation, the critical temperature for stability will be determined for each cluster species at neutron (low) and ion (high) damage rates.

Table 4.1: Input values used to calculate solute irradiation enhanced diffusion coefficients

Variable	Description	Value	Reference
a_0	lattice parameter	$3.58 \times 10^{-10} \text{ m}$	—
N_v	atomic number density	$8.72 \times 10^{28} \text{ at/m}^3$	—
G_{dpa}	Frenkel pair generation rate	$9.4 \times 10^{-6} \text{ dpa/s (neutron)}$	—
		$1.0 \times 10^{-3} \text{ dpa/s (ion)}$	
η	defect production efficiency	0.33	[229]
r_c	recombination radius	$5a_0$	[230]
D_v	diffusion coefficient for vacancies	$a_0^2(2 \times 10^{13} \text{ s}^{-1}) \exp\left(\frac{-1.2 \text{ eV}}{k_b T}\right)$	[213]
D_i	diffusion coefficient for interstitials	$a_0^2(2 \times 10^{13} \text{ s}^{-1}) \exp\left(\frac{-0.9 \text{ eV}}{k_b T}\right)$	[231]
c_v^{th}	thermal concentration of vacancies	$N_v \exp\left(\frac{-1.9 \text{ eV}}{k_b T}\right)$	[232]
D_{Cu}^{th}	Cu thermal diffusion coefficient	$(1.9 \times 10^{-5} \text{ m}^2/\text{s}) \exp\left(\frac{-273 \text{ kJ}}{R_g T}\right)$	[233]
D_{Ni}^{th}	Ni thermal diffusion coefficient	$(5.3 \times 10^{-4} \text{ m}^2/\text{s}) \exp\left(\frac{-318 \text{ kJ}}{R_g T}\right)$	[234]

First, the irradiation enhanced diffusion coefficient for each solute species is estimated by:

$$D^{irr} \approx D^{th} \left(\frac{c_v}{c_v^{th}} \right) \quad (4.3)$$

where D^{th} is the thermal solute chemical diffusion coefficient and c_v^{th} is the thermal concentration of vacancies. The concentration of vacancies under irradiation, c_v , was approximated assuming steady-state, recombination dominant conditions with:

$$c_v \approx \left(\frac{\eta G_{dpa} N_v}{4\pi r_c (D_v + D_i)} \right)^{1/2} \quad (4.4)$$

where G_{dpa} is Frenkel pair generation rate, η is defect production efficiency, N_v is atomic number density, r_c is recombination radius, D_v is the diffusion coefficient for vacancies, and D_i is the diffusion coefficient for interstitials. To simplify calculations, Cu for the Cu-rich clusters and Ni for the Ni-Si-Mn-rich clusters were assumed to be the diffusion limiting solute species. Values used in equations 4.3 and 4.4 are provided in Table 4.1.

The current international standard unit for energetic particle damage is dpa measured using the Norgett, Robinson, and Torrens (NRT) model [33]. However, NRT dpa only considers displacements and does not account for replacements (atoms transported from one lattice site to another). This is problematic as replacements contribute significantly to radiation mixing [235]. As a result, we have chosen to use recoils (displacements + replacements) per atom in lieu of NRT dpa. Cluster chemistry also needs to be considered when calculating the number of recoils for a specific solute species. For simplicity, the number of recoils for a given solute species is assumed to be proportional to solute content within the cluster, c_p . Thus, equation 4.2 is modified so that $q\phi$ is substituted with $c_p q\phi$, the recoil rate of a specific solute species, where q is the ratio of recoils to displacements and ϕ is the NRT damage rate. The value of q as well as the average recoil distance, λ , can be

Table 4.2: Input values used to calculate effective capillary radius under irradiation

Variable	Description	Value
c_p	concentration of solute in cluster	0.150 (Cu)
		0.315 (Ni)
q	ratio of recoils to displacements	40
ϕ	NRT damage rate	9.4×10^{-6} dpa/s (neutron)
		1.0×10^{-3} dpa/s (ion)
λ	mean recoil distance	$0.85a_0$
σ	interfacial energy	$0.05 - 0.15$ J/m ² (Cu)
		$0.2 - 0.5$ J/m ² (Ni)
V_m	molar volume of atoms in precipitate	7.09×10^{-6} m ³ /mol (Cu)
		7.20×10^{-6} m ³ /mol (Ni)
C_∞	solute concentration at the surface of a precipitate with infinite radius	$\frac{10^{(3.186-3083/T)}}{100}$ (Cu) [184]
		0.1 (Ni)

estimated from molecular dynamics simulations [236, 237]. The recoil distribution from a 10 keV cascade in Ni was fit with an exponential and then integrated up to a distance of 5 nm, roughly the radius of a cascade, to approximate the total number of recoil events. This value was then compared to the number of NRT displacements calculated with SRIM (quick Kinchin-Pease option and a displacement energy of 40 eV) using the damage energy method. Based on this analysis, q is approximately 40 recoils/displacement. In addition, the average recoil distance over the distribution was estimated as $0.85a_0$.

Interfacial energy is perhaps the most difficult parameter to estimate as it depends on several factors including crystallography misorientation, misfit strain, coherency, and solute segregation. Since Cu and austenite both have a face-centered cubic structure and the lattice parameter of pure Cu (3.61 Å) is nearly identical to that of austenite, the Cu-rich clusters are expected to be coherent. Bai et al. calculated using Lifshitz, Slyozov, and Wagner (LSW) theory the interfacial energy of Cu/ γ -Fe as 0.086 J/m² and Cu/Fe-18Cr-9Ni-3Cu as 0.017 J/m² [238]. On the other hand, Hirata and Hirano obtained a Cu/ γ -Fe interfacial energy of 0.14 J/m² [239]. And so, instead of a fixed value, the current analysis uses interfacial energies ranging from 0.05 J/m² to 0.15 J/m² for the Cu-rich clusters. Although G-phase also has a fcc structure, it has a significantly larger lattice parameter (11.1 Å) compared to austenite. Given this severe misfit, the interface between austenite and fully mature G-phase is expected to be incoherent. However, during nucleation before a cluster undergoes structural transformation, the interface may initially be coherent or semi-coherent. An interfacial energy of 0.2 J/m² is the upper bound expected for coherent interfaces, while an interfacial energy of 0.5 J/m² is the lower bound expected for incoherent interfaces [240]. Thus, an interfacial energy range of 0.2 J/m² to 0.5 J/m² was used in the current analysis for Ni-Si-Mn-rich clusters to reflect possible variation in coherency over the course of irradiation.

Cluster stability was evaluated with the modified Heinig model for both neutron and ion damage rates, assuming initial clustering based on the 5.4 dpa BOR-60 experimental data. At this starting condition, the Cu- and Ni-Si-Mn-rich clusters contained ~ 15 at.% Cu and ~ 31.5 at.% Ni, respectively. Also, since the Ni-Si-Mn-rich clusters are radiation induced, and negligible depletion of Ni near the cluster interfaces was measured with proximity histograms, C_∞ for these clusters was assumed to be equal to the bulk Ni concentration (≈ 10 at.%). The values used to calculate r_{cap}^{irr} with equations 4.1 and 4.2 are summarized in Table 4.2. Results as a function of irradiation temperature are plotted in Fig. 4.19. In general, r_{cap}^{irr} increases monotonically with temperature, and increasing damage rate causes the behavior to shift to higher temperatures. For the Cu-rich clusters, r_{cap}^{irr} becomes positive at temperatures $> 283 - 313$ °C for a damage rate of 9.4×10^{-7} dpa/s. This is consistent with the continued development of Cu-rich clusters observed during neutron irradiations at 318 °C when dose increased from 5.4 to 47.5 dpa. On the other hand, for a damage rate of 1×10^{-3} dpa/s, r_{cap}^{irr} becomes positive for the Cu-rich clusters at temperatures $> 390 - 434$ °C. Since in our experiments the Cu-rich clusters dissolved during ion irradiations at 380 – 420 °C, it is likely that the true interfacial energy for the clusters at 5.4 dpa in this alloy is closer to 0.05 J/m² than to 0.15 J/m². Further, λ is seemingly less than the critical relocation distance, R_c , of this material given that no inverse coarsening was observed. However, there is also the remote possibility that inverse coarsening during ion irradiations caused the Cu-rich clusters to shrink below our APT cluster detection limit (~ 0.3 nm radius).

For the Ni-Si-Mn-rich clusters, r_{cap}^{irr} is positive at temperatures $> 235 - 258$ °C for a damage rate of 9.4×10^{-7} dpa/s. This agrees with our 318 °C neutron irradiation results, where nucleation and growth of the Ni-Si-Mn-rich clusters was seen from 5.4 to 47.5 dpa. For a damage rate of 1×10^{-3} dpa/s, r_{cap}^{irr} is positive for temperatures $> 339 - 374$ °C. The negligible growth of the Ni-Si-Mn-rich clusters after ion irradiation

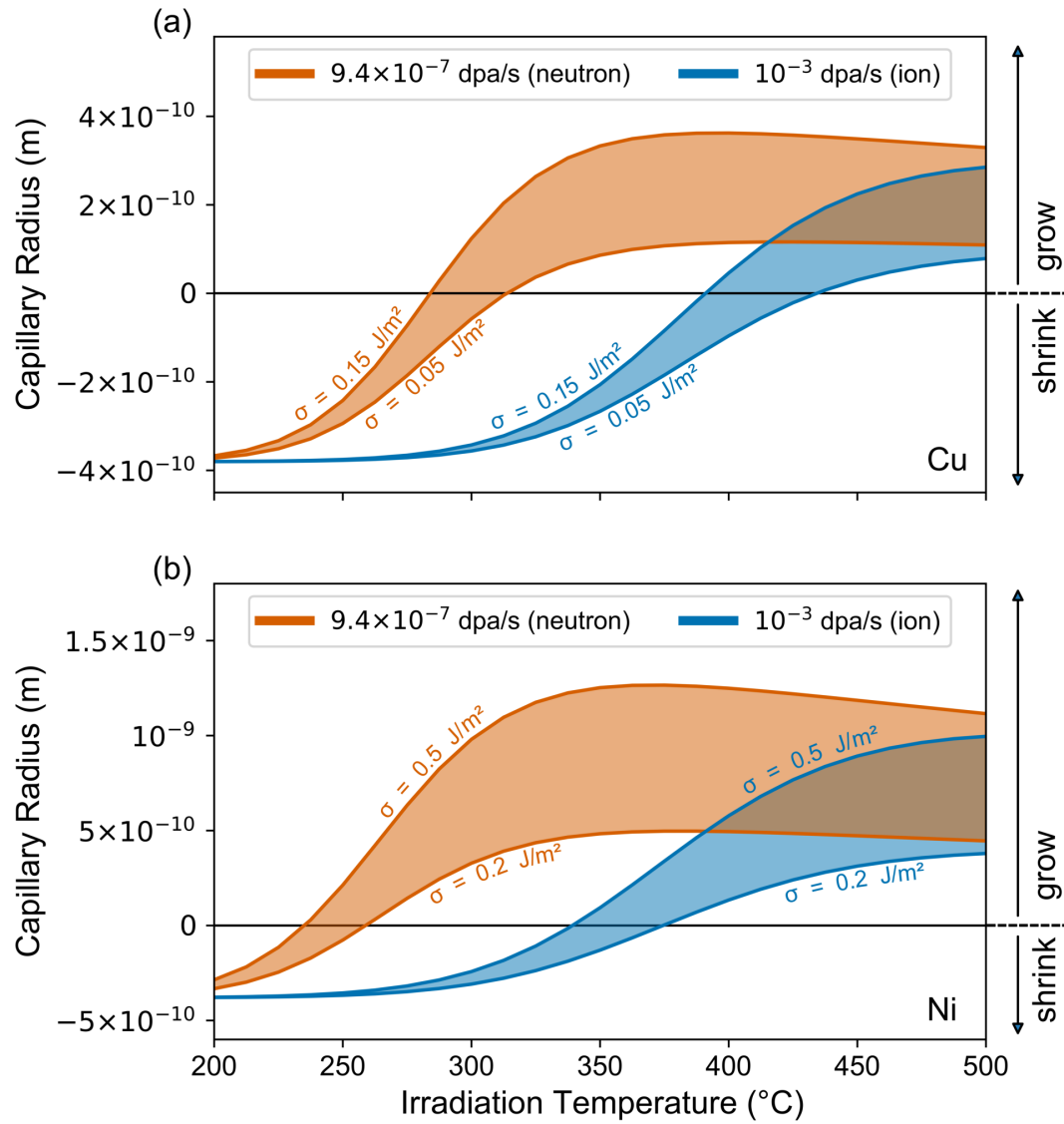


Figure 4.19: Effective capillary radius for (a) Cu in Cu-rich clusters and (b) for Ni in Ni-Si-Mn-rich clusters under irradiation as a function of temperature, calculated using the modified Heinig model.

at 380 °C is consistent with $r_{cap}^{irr} \approx 0$. At higher ion irradiation temperatures (400 and 420 °C), the Ni-Si-Mn-rich clusters readily nucleate and coarsen, which is congruent with the modeling that shows r_{cap}^{irr} is positive. It is worth noting given our assumption for C_∞ that if the Ni solubility limit is halved, the temperature ranges where $r_{cap}^{irr} > 0$ shift ~ 20 and 30 degrees higher for the neutron and ion irradiation damage rates, respectively.

Overall, the critical temperatures for cluster stability from the modified Heinig model agree well with our experimental data. Based on equations 4.1 and 4.2 and the modifications we introduced, r_{cap}^{irr} is positive when:

$$\frac{4r_{cap}D^{irr}C_\infty}{c_p} > 5q\phi\lambda^3 \quad (4.5)$$

The right-hand side of equation 4.5 captures the effect of radiation mixing, while the left-hand side describes a cluster's ability to reform after ballistic attack. We have assumed that the ratio of recoils to displacements (q), mean recoil distance (λ), and NRT damage rate (ϕ) for the neutron and ion irradiations are the same for both Cu-rich and Ni-Si-Mn rich clusters. This suggests that the difference in cluster stability observed during accelerated damage rate irradiation for the two cluster species is due to solute RED (D^{irr}), interfacial energy (σ), molar volume (V_m), solubility (C_∞), and/or cluster chemistry (c_p). While RED influences the kinetics of solute recovery after ballistic ejection, interfacial energy, molar volume, solubility, and cluster chemistry all shape the solute concentration gradient near the cluster interface, and therefore, the thermodynamic force driving the restoring solute flux. Because D_{Cu}^{irr} is greater than D_{Ni}^{irr} , Cu ejected from Cu-rich clusters should be able to diffuse back faster than Ni ejected from Ni-Si-Mn-rich clusters. If RED alone was responsible for cluster stability, the Cu-rich clusters would in principle be more stable than the Ni-Si-Mn-rich ones. However, our experimental results indicate otherwise, and so it appears that the concentration gradient near the cluster

interface is instrumental to solute recovery. Since the parameters of interfacial energy, molar volume, thermal equilibrium solubility, and cluster chemistry are independent of irradiation, this indicates different cluster species may have innately different susceptibilities to ballistic dissolution.

It should be noted that in explaining cluster evolution with the Heinig model, we did not consider any flux coupling between point defects (vacancies and interstitials) and solute atoms. In general, solute-point defect flux couplings are significant for precipitates that are radiation-induced, but may be negligible for precipitates that are radiation-enhanced. In the fcc Fe-Cr-Ni system, Ni-Si enrichment at dislocations, discussed previously, provides evidence of solute-point defect flux coupling. Si is known to have a positive flux coupling, since it binds and migrates with self interstitial atoms [213]. By contrast, Fe, Cr, and Ni likely have a negative flux coupling with vacancies as they migrate via the inverse Kirkendall mechanism [212]. These solute-point defect flux couplings may help stabilize the Ni-Si-Mn-rich clusters because they provide an additional pathway for constituent elements to be replenished after ballistic ejection. On the other hand, no RIS of Cu was detected on microstructural defects (dislocations, grain boundaries, etc.). It is therefore likely that Cu does not couple strongly with either point defect flux in the fcc Fe-Cr-Ni system. Consequentially, no supplemental source of solute may aid the Cu-rich clusters under ballistic attack.

Besides neglecting solute-point defect flux couplings, it is also important to recognize that the Heinig model is limited in the sense that it only provides insight into whether an existing precipitate is likely to grow or shrink when exposed to a given irradiation condition. Provided all inputs are well-defined and robust, this model can be used to identify the critical temperature ranges where clusters are expected to be stable for a certain dose rate. It should be noted that the Heinig model does not provide coarsening or dissolution rates, which can be used to predict

steady state precipitate microstructure. In fact, cluster radius and number density do not influence r_{cap}^{irr} (see equations 4.1 and 4.2). However, solubility at the cluster interface will be modified by cluster radius based on the Gibbs-Thomson effect. The impact of cluster size on coarsening or dissolution kinetics is therefore only loosely captured by the Heinig model.

The Heinig model also does not address chemical or structural stability and the nucleation stage of precipitation. As a result, it cannot explain the discrepancies we observed between the Ni-Si-Mn-rich clusters after 42 dpa ion irradiation and 47.5 dpa neutron irradiation. After ion irradiation at 380 °C, the composition of the clusters was significantly different from the neutron case, even though average radius and number density were alike. By contrast, after ion irradiation at 400 and 420 °C, the composition of the clusters was similar to the neutron case while average radius and number density were higher and lower, respectively. To rationalize these results, advanced models are needed. In some cases, further model development is also required, for example, to understand the effect of irradiation damage rate on precipitate nucleation. The limited scope of the Heinig model undoubtedly highlights that a single, comprehensive model covering all aspects of irradiation phase stability remains elusive.

4.3 Conclusions

In this study, APT was used to characterize solute nanoclusters in a 304L austenitic stainless steel that was irradiated by fast neutrons ($E > 0.1$ MeV) in the BOR-60 reactor at 318 °C and subsequently by self-ion irradiations. Starting with neutron irradiated 5.4 dpa samples, ion irradiations were performed at 380, 400, and 420 °C. For 380 °C irradiations, added ion doses were 4.7 and 42 dpa to reach total neutron plus ion doses of 10.1 and 47.4 dpa. For 400 and 420 °C

irradiations, 42 dpa ion dose was added to reach a total neutron plus ion dose of 47.4 dpa.

The distinct Cu- and Ni-Si-Mn-rich nanocluster populations that formed during BOR-60 neutron irradiation and then were modified by ion irradiation, exemplify the complex manner in which damage rate influences phase stability. The formation of Cu-rich nanoclusters was enhanced by neutron irradiation. However, after ion irradiation at temperatures between 380 – 420 °C, the Cu-rich clusters were ballistically dissolved. On the other hand, Ni-Si-Mn-rich nanoclusters were less affected by ballistic dissolution. By the highest neutron dose of 47.5 dpa, Ni-Si-Mn-rich clusters coarsened into G-phase precipitates. When 42 dpa was added by ion irradiation at 380 °C to the 5.4 dpa neutron irradiated sample, the Ni-Si-Mn-rich clusters remained stable, but showed no signs of further evolution. For ion irradiations at 400 and 420 °C, the Ni-Si-Mn-rich clusters matured into a low density of large G-phase precipitates with no significant ballistic dissolution. Even though the chemistry of the Ni-Si-Mn-rich clusters after ion irradiation at 400 and 420 °C was close to the neutron irradiation case, cluster sizes were larger and number densities were lower, which illustrates the stark differences between the evolution of solute nanoclusters during high and low dose rate particle bombardment. In nuclear materials, emulating cluster or precipitate microstructures formed during neutron irradiation with accelerated damage rate ion irradiation remains a significant challenge. In this case, even with the Cu- and Ni-Si-Mn-rich nanoclusters partially nucleated by neutron irradiation, high damage rate ion irradiation clearly altered the later stages of development.

The experimental results for both Cu- and Ni-Si-Mn-rich clusters were consistent with predictions for Ostwald ripening or ballistic dissolution/inverse coarsening by the modified Heinig model. The model, which contains the mechanisms of RED and ballistic dissolution, can be used to identify the critical temperature

and dose rate ranges for precipitate stability. For ion beam fabrication of nanocomposites, identifying such critical temperatures and dose rates can facilitate the selection of optimal processing conditions. Analyzing the experimental and modeling results together revealed that solute concentration gradient near the cluster interface plays an important role in phase stability and explains the contrasting behavior of the Cu- and Ni-Si-Mn-rich clusters under high damage rate irradiation. Since the parameters that influence this concentration gradient (interfacial energy, molar volume, thermal equilibrium solubility, and cluster chemistry) are independent of irradiation, different nanocluster species can have different characteristic susceptibility to ballistic dissolution under the same energetic particle bombardment conditions. This insight into radiation phase stability underscores that for the design and production of nanostructured materials, it is necessary to evaluate the thermodynamic driving force stabilizing each individual nanoprecipitate, nanodispersoid, or solute nanocluster species.

Chapter 5

Contribution of phase instabilities to hardening in ODS alloys

The fracture toughness of non-irradiated ODS alloys is subpar, thus any further deterioration of this property under irradiation is a primary concern for the low temperature operation of thick-walled components. In bcc metals, an indicator of impact toughness and by extension fracture toughness is the ductile to brittle transition temperature (DBTT). Given the relationship between shift in DBTT and radiation hardening described by Ludwig and Davidenkov, it is therefore important to quantify the magnitude of any hardening under irradiation. It has not been well established whether ODS alloys have similar low temperature hardening and embrittlement behavior as RAFM steels, or if there are any peculiarities. As a result, the mechanical properties of 12YWT, MA957, and PM2000 neutron irradiated to 5.0 – 23.3 dpa over temperatures varying between 335 and 500 °C were measured with Vickers microhardness and uniaxial tensile tests. Then, solute nanoclustering in PM2000 and MA957 was characterized by APT and TEM. Specific focus was placed on comparing the mechanical properties and microstructure of neutron-irradiated

MA957 to understand the contribution of phase instabilities to hardening in ODS alloys.

5.1 Results

5.1.1 Irradiation hardening and loss of ductility

Vickers microhardness indentation tests

Vickers microhardness indentation tests were performed in the hotcell at room temperature on the HFIR irradiated ODS alloys, using 1 kg load and 15 s dwell time, in accordance with ASTM E384 Standard Test Method for Microindentation Hardness of Materials. As detailed in Section 3.4, the tests were performed on the undeformed head/grip section of the SS-J3 tensile samples prior to performing tensile tests, with at least 8 indents per specimen. For an irradiation temperature of 335 °C, Figure 5.1 plots the hardness of PM2000, MA957, and 12YWT as a function of neutron dose. All the alloys showed significant increase in hardness as compared to their non-irradiated values, highlighting their susceptibility to irradiation hardening. For 12YWT, the difference between hardening at 5.0 dpa versus ~ 13.1 dpa was similar, indicating that hardening may have saturated already. However, clear evidence of hardening saturation at such low doses was not evident for MA957. Alloy PM2000 showed the highest relative increase in hardness around $\sim 5 - 5.5$ dpa. Due to absence of data at higher doses, it is difficult to say if the behavior of this alloy would be qualitatively similar to 12YWT/MA957 or not.

Figure 5.2 plots the results of hardening as a function of irradiation temperature. The figure also compares the present results with data on literature on hardness of RAFM steels after neutron irradiation to doses less than ~ 15 dpa. Surprisingly, all three ODS alloys continued to show irradiation hardening at the elevated irradiation temperatures of 450 and 500 °C, where RAFM steels do not harden substantially.

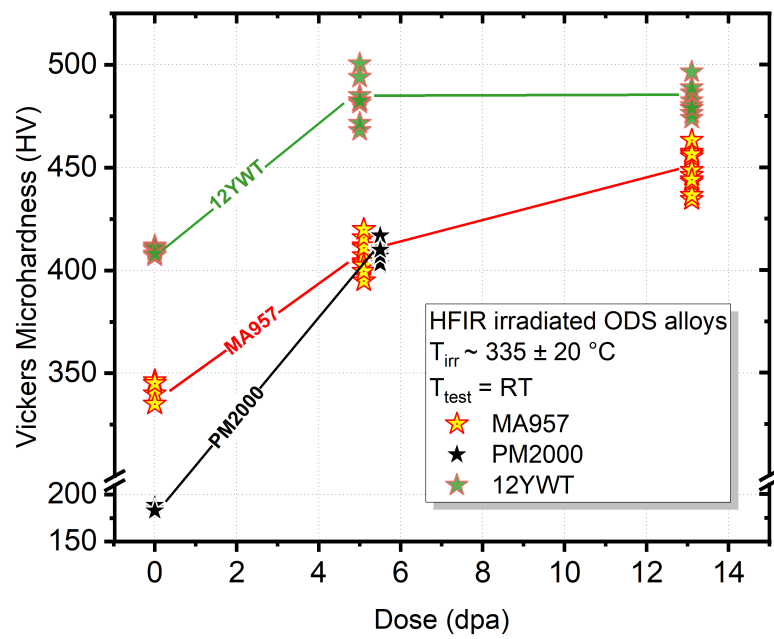


Figure 5.1: Irradiation hardening versus neutron dose for ODS alloys irradiated in HFIR at $\sim 335^{\circ}\text{C}$ measured using Vickers microhardness indentation testing. Vickers microhardness values may be converted to MPa by multiplying by 9.8.

Between ~ 300 to 450°C , hardness of all three alloys did not recover much, showing an almost flat trend line. For the 500°C irradiation temperature, irradiation hardening reduced but never fully recovered to non-irradiated values. Furthermore, none of the alloys showed signs of softening at such high temperatures, which is a phenomenon that is typically well-known for RAFM steels [7]. To confirm the results of indentation testing, uniaxial tensile tests were performed. The results of those tests are discussed in the next subsection.

Uniaxial tensile tests

With guidance from ASTM E8 Standard Test Methods for Tension Testing of Metallic Materials, tensile tests were performed at hotcell on HFIR irradiated SS-J3 samples of the ODS alloys. Tests were performed at room temperature with a strain rate of 10^{-3} s^{-1} ($5 \times 10^{-3}\text{ mm/s}$). Because the irradiated PM2000 alloys typically failed in the elastic load-line region, here only the results from MA957 and 12YWT are reported.

Figure 5.3 shows the engineering stress-strain curves of MA957 and 12YWT irradiated at 335°C . In agreement with hardness results, Figure 5.3 highlights irradiation hardening in these two alloys for neutron dose up to ~ 13.1 dpa. Hardening was accompanied by loss in uniform and total elongations. However, the stress-strain curves of these two alloys were quite different to each other. For MA957, despite a significant increase in yield stress (σ_{YS}) there was considerable uniform elongation left up to the highest studied dose of ~ 13.1 dpa. 12YWT demonstrated stress-strain curves that were more akin to FM steels [7, 13, 241] having two key noticeable features: (i) initially severe uniform elongation loss and (ii) the primary ductility remaining in the alloys post irradiation (i.e. ductility post uniform elongation). The 12YWT samples irradiated to 13.1 dpa, however, showed appreciably less post-uniform elongation ductility than the samples irradiated to

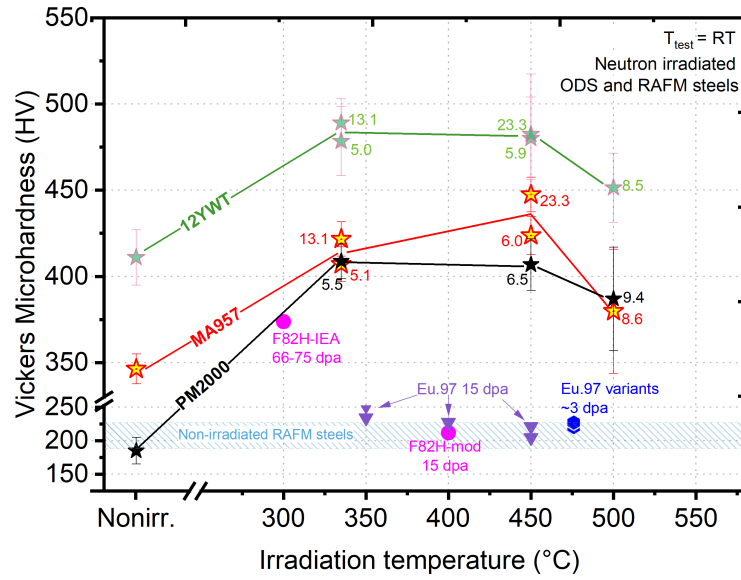


Figure 5.2: Hardening in HFIR irradiated ODS alloys measured using Vickers microhardness indentation testing. Vickers microhardness values may be converted to MPa by multiplying by 9.8. $T_{\text{irr}} = 335 - 500^\circ\text{C}$ and $5.1 - 23.3$ dpa. Part of these results are now published in Ref. [7]. The dpa values are annotated in the figure. For comparison, hardness results from F82H-IEA, F82H-mod and Eurofer97 variants are overlaid with RAFM data points added from [10, 11, 12, 13].

only 5.0 dpa. Figure 5.4 plots σ_{YS} as a function of neutron dose for the two studied alloys. For comparison, the Figure 5.4 also plots data from literature on irradiation hardening of MA957 bars studied in CEA-Saclay following irradiations in OSIRIS and BOR60 reactors [14, 15, 16]. Moreover, to draw contrast between ODS alloys and RAFM steels, relatively new data produced at ORNL on σ_{YS} increase of different F82H steel variants after irradiations in HFIR [12] are also plotted in the same figure. For both 12YWT and MA957 in this study, the initial increase in σ_{YS} as compared to non-irradiated values is evident. After that, not much change in σ_{YS} occurred at the higher dose for 12YWT. This is consistent with Vickers hardness data plotted in Figure 5.1 suggesting a saturation, although higher dose data will be needed to fully confirm if saturation occurred or not. The MA957 evaluated in our present study showed a continuous increase of σ_{YS} , with no evidence of saturation, concurring results from indentation testing shown in Figure 5.1. There were slight differences in performance between the MA957 samples extracted from thick-walled tube studied in our research versus MA957 alloy from extruded bars that were irradiated in BOR60 and OSIRIS [12]. This is expected because the microstructures of the bars versus tubes are expected to be different. The bar samples were initially slightly softer than the tubes, hence the curve showing σ_{YS} is shifted lower. But the rate of hardening does not appear to be dramatically different as compared to their starting σ_{YS} . It is interesting to note that BOR60 data on MA957 suggests hardening saturation may occur after ~ 40 dpa. High dose data from HFIR will be needed in future studies to confirm this behavior.

The uniform plastic (UEp) and total plastic (TEp) elongations as a function of neutron dose are plotted in Figure 5.5. The results were very different between MA957 and 12YWT. The 12YWT alloy showed RAFM steel-like behavior, where there was a dramatic drop in UEp at relatively low doses and after that the UEp seems to have saturated at low values around 0.4 – 0.5%. The drop in UEp of 12YWT

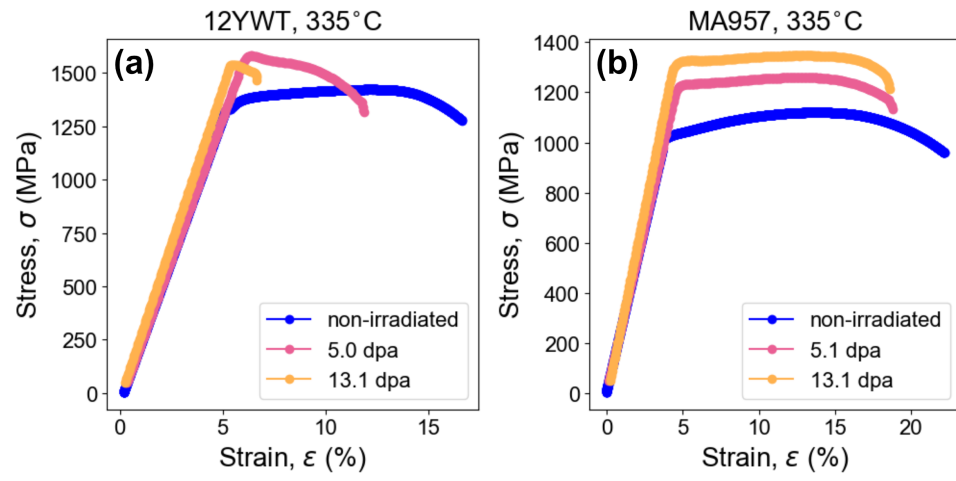


Figure 5.3: Engineering stress-strain curves of (a) 12YWT and (b) MA957 before and after irradiation at 335 °C.

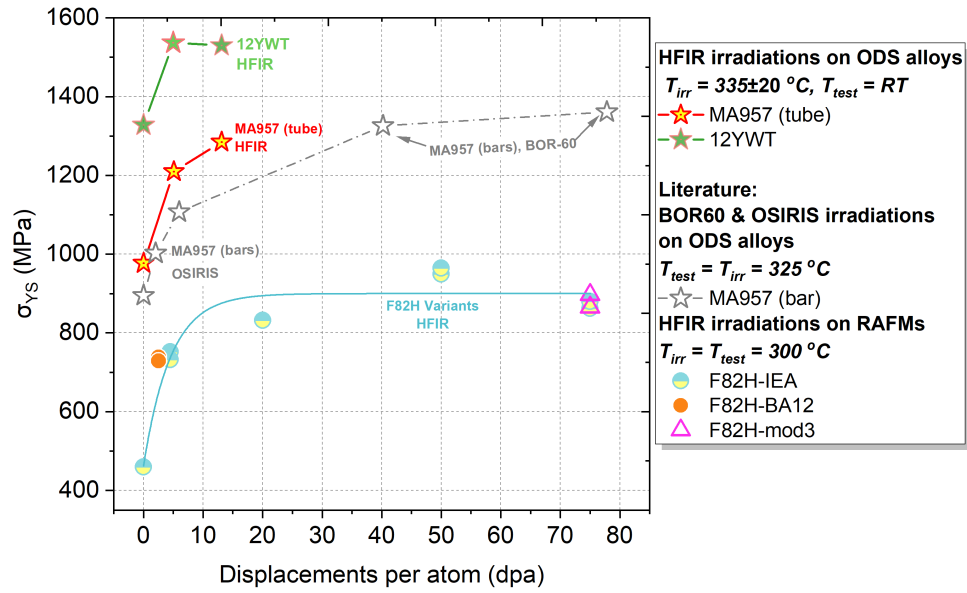


Figure 5.4: The yield stress (σ_{YS}) as a function of dose for neutron irradiations around 300 – 335 °C. The present results from HFIR on 12YWT and MA957 are plotted with literature data on MA957 (bars) following irradiations in OSIRIS and BOR60 reactors [14, 15, 16]. Literature data on F82H variants after HFIR irradiations are plotted using Ref. [12].

with dose was qualitatively similar to the UEp loss trend of HFIR irradiated F82H variants. For MA957, the UEp loss was more gradual. The initial decrease in UEp at low doses (~ 5 dpa) was not nearly as significant as that for 12YWT or F82H, suggesting better performance in terms of ductility. By comparison, the MA957 bars irradiated in OSIRIS and BOR60 showed lower UEp values both in non-irradiated and irradiated conditions, and the results also suggest the UEp of such alloys may drop to very low values ($\sim 1\%$) at doses > 75 dpa. Better understanding of the high dose trend requires further HFIR neutron irradiation experiments.

In terms of TE_p, Figure 5.5 reveals that TE_p of HFIR irradiated 12YWT decreased continually with dose. At the highest studied dose of 13.1 dpa, the TE_p reduced to less than 4.5 % as compared to $>14 - 15\%$ in the nonirradiated condition, with no signs of saturation. This demonstrates significantly worse ductility performance as compared to MA957 at low doses. The overall TE_p performance of 12YWT is even poorer as compared to RAFM steels which typically maintain total elongations above $\sim 5\%$ up to 70 – 80 dpa [7]. The MA957 irradiated in HFIR showed better TE_p as compared to M957 bars irradiated in BOR60/OSIRIS. This is expected because the processing of these two alloys were completely different, that would produce very different microstructures. Overall, the MA957 samples taken from tubes irradiated in HFIR showed better properties as compared to MA957 samples taken from bars irradiated in BOR60/OSIRIS. The high dose data on TE_p loss of MA957 from tubes after HFIR irradiations is clearly missing, but BOR60 data suggests that even though this alloy starts with relatively higher ductility, the TE_p may reduce to much smaller values than typical RAFM steel values for doses $> 70 - 80$ dpa.

The engineering stress-strain curves of 12YWT and MA957 after neutron irradiations in HFIR at ~ 450 and 500°C are plotted in Figure 5.6. What is interesting to note is that even at such high temperatures, both these alloys showed

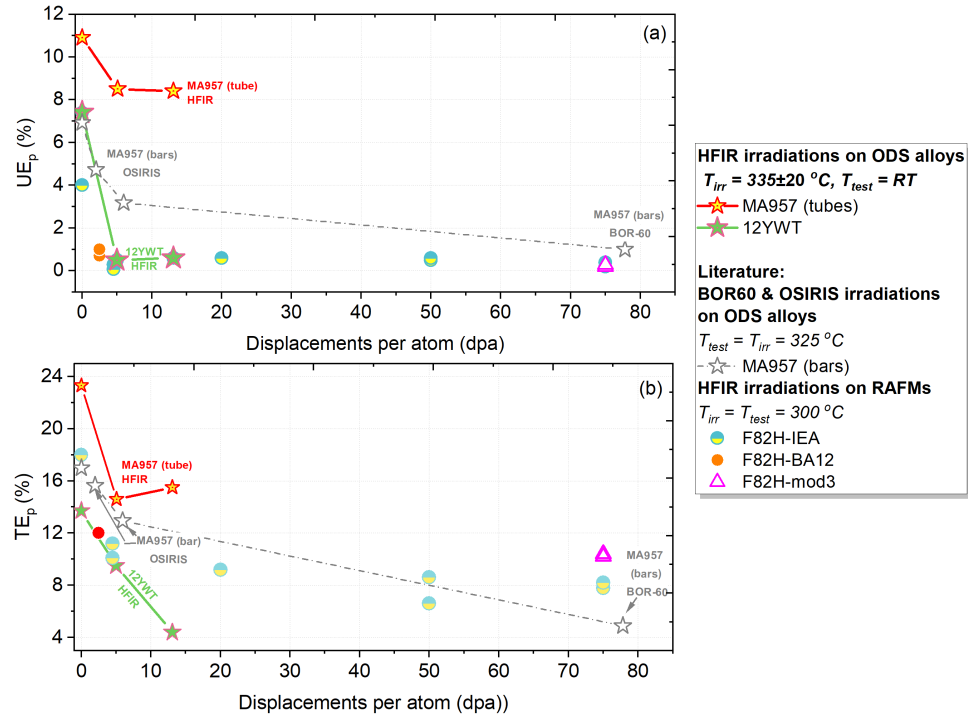


Figure 5.5: Uniform and total plastic elongations of HFIR irradiated MA957 and 12YWT as a function of neutron dose. Literature data on MA957 (bars) following irradiations in OSIRIS and BOR60 reactors are taken from Ref. [14, 15, 16]. Literature data on F82H variants after HFIR irradiations are plotted using Ref. [12].

significant increase in σ_{YS} and loss of ductility. Figure 7 shows the increase in $\Delta\sigma_{YS}$ as a function of irradiation temperature. For reference, this figure also presents data from literature on different RAFM steels such as Eurofer97, F82H and JLF-1 that were irradiated to similar conditions. Collectively, Figure 5.7 (and Figure 5.2) reveal that ODS alloys such as 12YWT and MA957 continue to show hardening at high temperatures of 450 and 500 °C where RAFM steels do not show irradiation hardening. At 500 °C, hardening in both the alloys decreases. But full recovery to non-irradiated values was not achieved. Between 335 and 450 °C, $\Delta\sigma_{YS}$ in the two alloys remained almost similar with no signs of hardening recovery. This is concerning from the point of view of applicability of these alloys in new reactor concepts such as fusion, where different lower temperature limit maybe necessary as compared to RAFM steels. MA957 showed higher hardening as compared to 12YWT, which will be shown in the next sections is related to the higher concentration of embrittling Cr-enriched cluster formation. The UEp and TEp measured at RT of both alloys did not change drastically with irradiation temperature (see Table 5.1).

5.1.2 Solute nanoclustering during neutron irradiation

Effect of temperature and dose on solute nanoclustering in PM2000

Both APT and TEM were used to analyze solute nanoclustering in the HFIR-irradiated PM2000 samples. Because the dispersoids in PM2000 were too large to be captured in the APT needles, solute nanoclustering in the matrix was the focus of APT characterization. APT reconstructions were done with Cameca's IVAS and the OSCAR program was used for cluster identification and analysis. To determine which species were clustered, the local solute concentration around each atom was calculated for a fixed radius corresponding to ~ 100 atoms. The real local chemistry frequency distribution was then compared to a randomized dataset. Figure 5.8

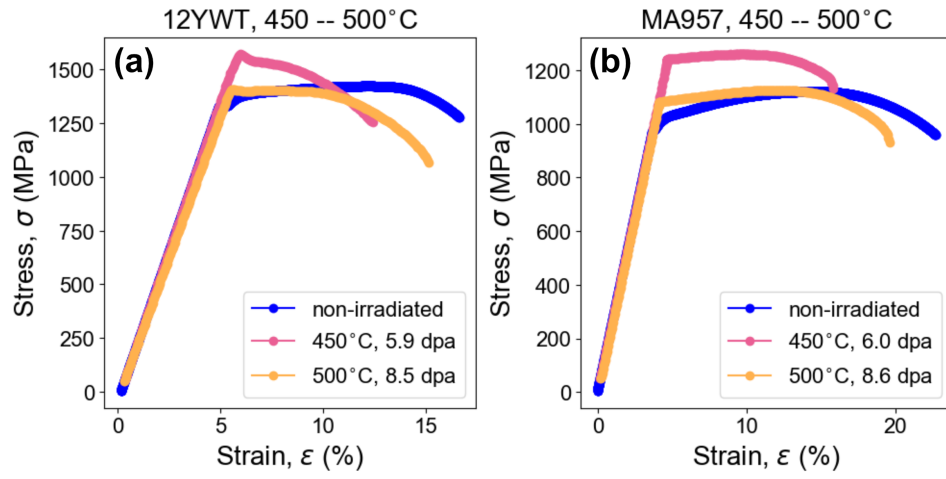


Figure 5.6: Engineering stress-strain curves of (a) 12YWT and (b) MA957 before and after irradiation in HFIR at 450 and 500 °C.

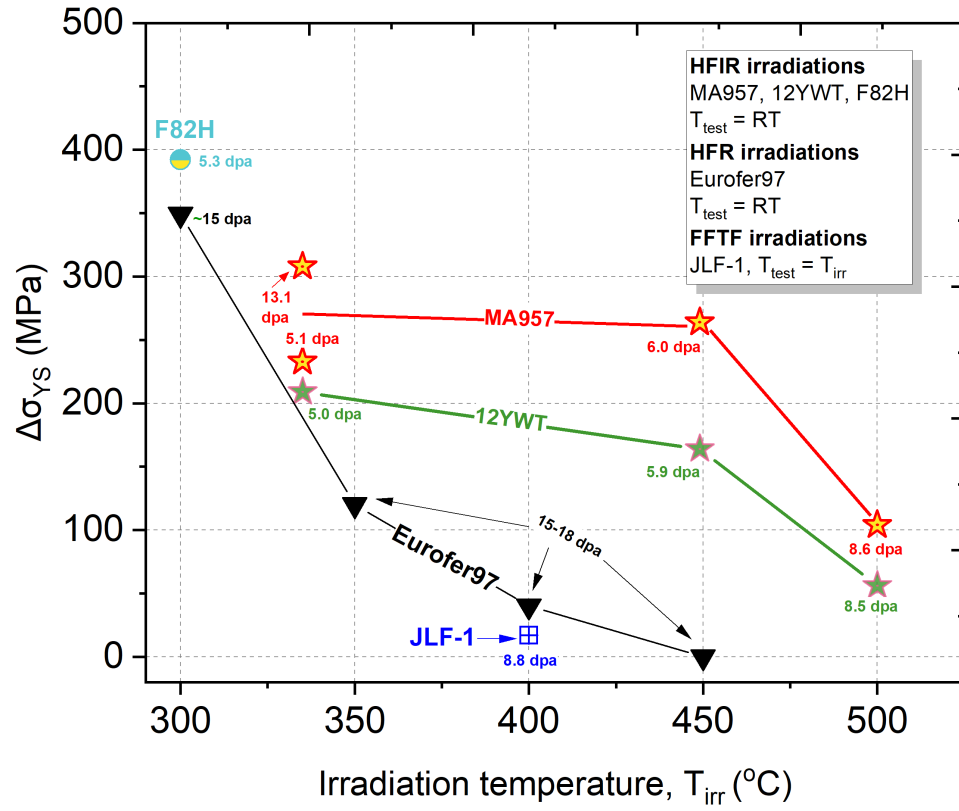


Figure 5.7: Increase in yield stress of HFIR irradiated 12YWT and MA957 as a function of irradiation temperature. RAFM steels data from literature is overlaid from Refs. [17, 18, 19, 20].

Table 5.1: Summary of tensile properties of nonirradiated and HFIR irradiated ODS alloys

Experiment	Material	IDs	Target dose (dpa)	T_{irr} (°C)	T_{test} (°C)	σ_{YS} (MPa)	σ_{UTS} (MPa)	UEp (%)	TEp (%)	σ_{UTS}/σ_{YS}
Nonirr.	12YWT	—	0	—	24	1328	1445	7.4	13.7	1.09
JP26	12YWT	ZP01	5.0	335	24	1537	1582	0.50	9.50	1.03
JP26	12YWT	ZP10	5.9	450	24	1492	1572	0.50	8.80	1.05
JP26	12YWT	ZP21	8.5	500	24	1384	1408	0.40	12.70	1.02
JP27	12YWT	ZP30	13.1	335	24	1530	1540	0.60	4.40	1.01
Nonirr.	MA957	—	0	—	24	977	1114	10.9	23.3	1.14
JP26	MA957	ZQ01	5.1	335	24	1210	1260	8.50	14.60	1.04
JP26	MA957	ZQ10	6.0	450	24	1241	1261	6.10	12.50	1.02
JP26	MA957	ZQ21	8.6	500	24	1081	1126	8.80	18.80	1.04
JP27	MA957	ZQ30	13.1	335	24	1285	1345	8.40	15.50	1.05
JP26	PM2000	ZR21	8.7	500	24	879	890	0.08	2.20	1.01

shows the results for Al, Cr, and Ti at the 5.5 – 9.4 dpa, 335 – 500 °C irradiation conditions. At 450 °C and below, only Cr atoms appeared to be clustered, as the deviation between the real and random distributions for Al and Ti were insignificant. However, at 500 °C, Cr, Al, and Ti all appeared to be clustered.

Based on examination of the reconstructions, the Al and Ti clustering at 500 °C appeared to be spatially correlated. Thus, two cluster species were observed: Cr-enriched and Al-Ti-enriched. The search parameters for each cluster species are provided in Table 3.9. The Cr-enriched and Al-Ti-enriched clusters were identified based on Cr and Ti ions, respectively. Figure 5.9 shows representative APT needles from each condition, where the solute atom maps and the associated clusters are highlighted. Note that any Ti clusters detected at 335 and 450 °C were considered stochastic noise.

Cr-enriched clusters were observed in each sample of PM2000 after irradiation between 335 and 500 °C. Figure 5.10 presents the size distributions; size, number density, and sink strength trends; and the composition of the cluster cores with irradiation temperature. At 450 °C and below, the size and composition of the Cr-enriched clusters remained consistent. The average Guinier radius of the Cr-enriched clusters was 1.4 ± 0.7 nm and 1.6 ± 0.9 nm after irradiation at 335 and 450 °C, respectively. The average core composition of the clusters was 46.6 ± 7.6 at.% Cr and 43.0 ± 7.5 at.% Fe. However, the number density of Cr-enriched clusters steeply declined as irradiation temperature increased, even up to 500 °C. As a result, the sink strength of the Cr-enriched clusters also monotonically decreased with irradiation temperature. The percentage of Cr atoms partitioned into clusters was < 10 % at 335 and 450 °C. By comparison, after irradiation at 500 °C a significantly higher percentage of Cr atoms, ~ 25 %, were partitioned into clusters. The concentration of Cr in the matrix also decreased from ~ 15.9 to 13.3 at 335 °C and 500 °C, respectively. The higher fraction of clustering manifested as an increase

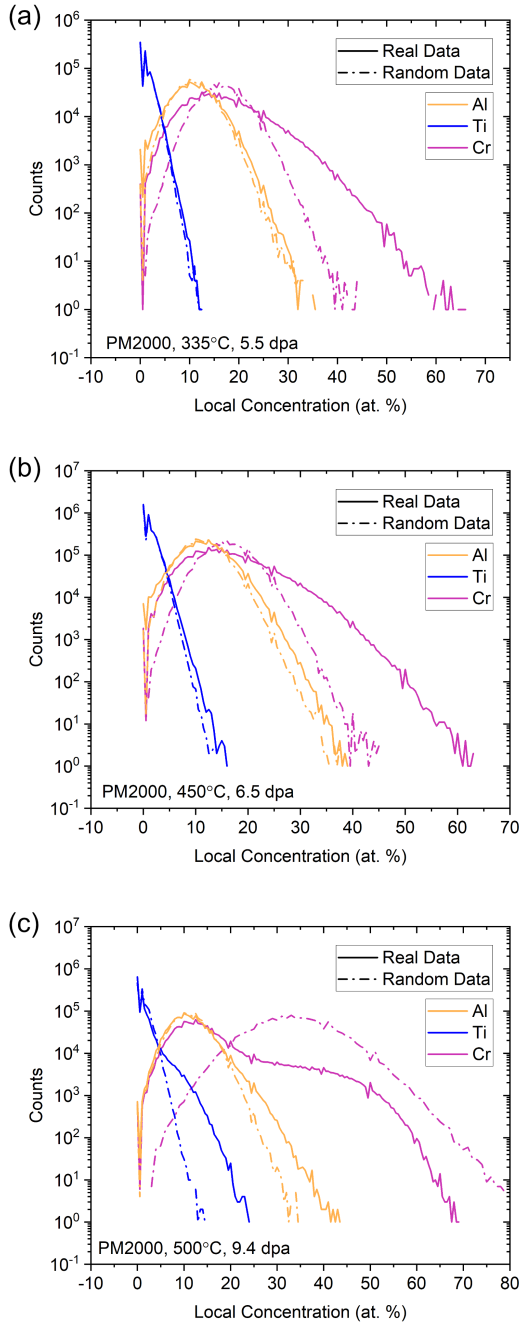


Figure 5.8: A comparison of the real and random local chemistry frequency distributions for PM2000 irradiated at (a) 335 °C, 5.5 dpa, (b) 450 °C, 6.5 dpa, and (c) 500 °C, 9.4 dpa.

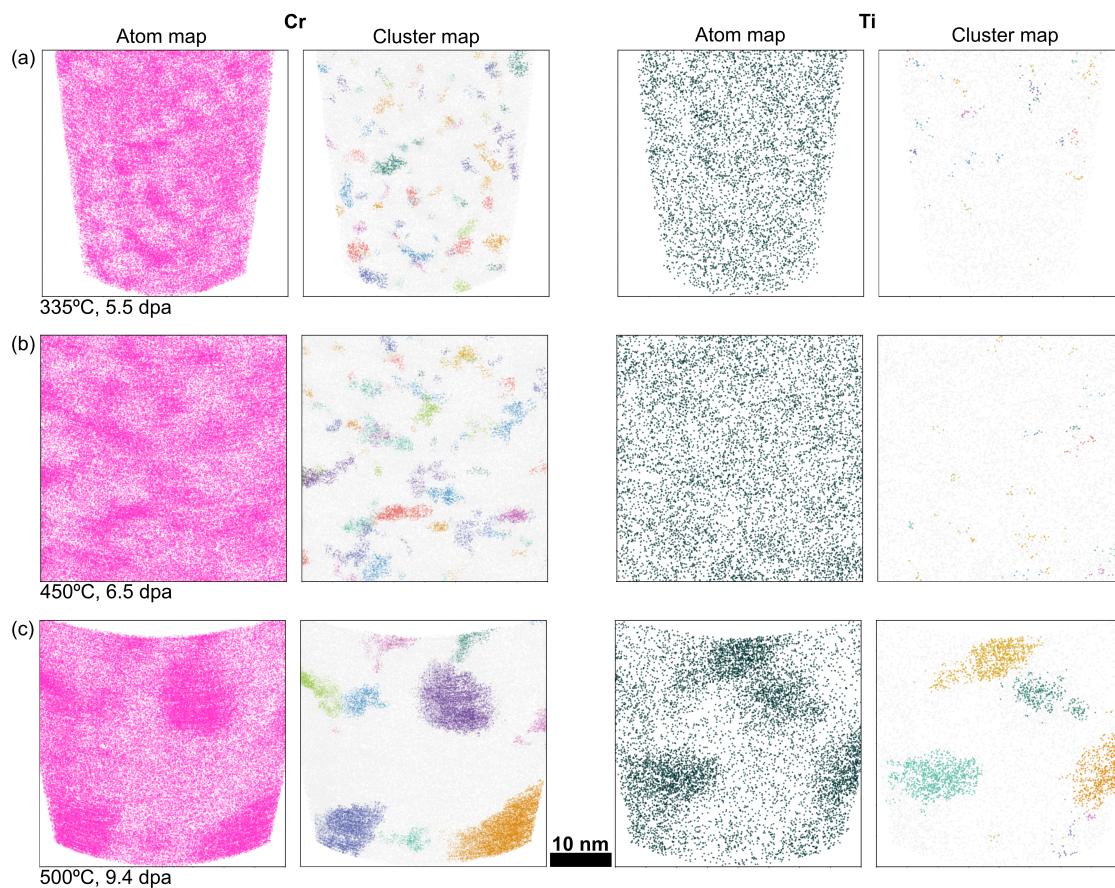


Figure 5.9: Atom and cluster maps of representative volumes from PM2000 after neutron irradiation at (a) 335 °C, 5.5 dpa, (b) 450 °C, 6.5 dpa, and (c) 500 °C, 9.4 dpa. Maps for Cr and Ti are shown. Sample volume are 40 x 40 x 15 nm each.

in size and Cr content of the clusters. Unfortunately, due to the large size of the clusters at 500 °C, the number of clusters captured in a needle was low and statistics were poor. The average Cr content in the clusters increased slightly to 52.7 ± 7.6 at. %. However, the change in concentration from 450 °C was within error. The average Guinier radius of the clusters was 5.3 ± 4.3 nm. However, this cluster size is likely to be a misrepresentation, since many of the Cr-enriched clusters in the 500 °C condition were non-spherical and elongated in a particular direction. Unfortunately, this crystallographic direction could not be identified by APT due to the limited crystallographic information visible in the desorption maps. Also, many of the clusters were only partially captured in the needle volume. As will be discussed later, TEM was used to better understand these features.

Clustering of Al and Ti was not pervasive over the 335 – 450 °C temperature range. However, at 500 °C, Al and Ti jointly cluster adjacent to Cr-enriched regions. The size, number density, and sink strength of the Al-Ti-enriched clusters were comparable to the Cr-enriched ones. The average Guinier diameter of the Al-Ti-enriched clusters was 4.9 ± 4.4 nm. Again, error in size was large due to the low number density ($2.1 \times 10^{23} \text{ m}^{-3}$) of clusters intercepted in the needles. The average core composition of the clusters reached 47.3Fe-27.3Cr-17.8Al-7.0Ti at.%. Thus, Cr appeared enriched in the clusters as well.

Because the size of the Cr- and Al-Ti-enriched clusters at 500 °C appeared to be too large to adequately measure with APT, STEM-EDS was used as a complementary characterization technique. A STEM-EDS map from the PM2000 500 °C irradiation condition quantified by weight percent is shown in Figure 5.11a with Cr in pink, Al in light blue, and Ti in dark blue. The STEM-EDS map was collected from a grain oriented along the $\langle 100 \rangle$ zone axis, and therefore the linear features that Cr appears to be segregated on are dislocations. A selected area diffraction pattern collected from the region with conventional TEM is shown in

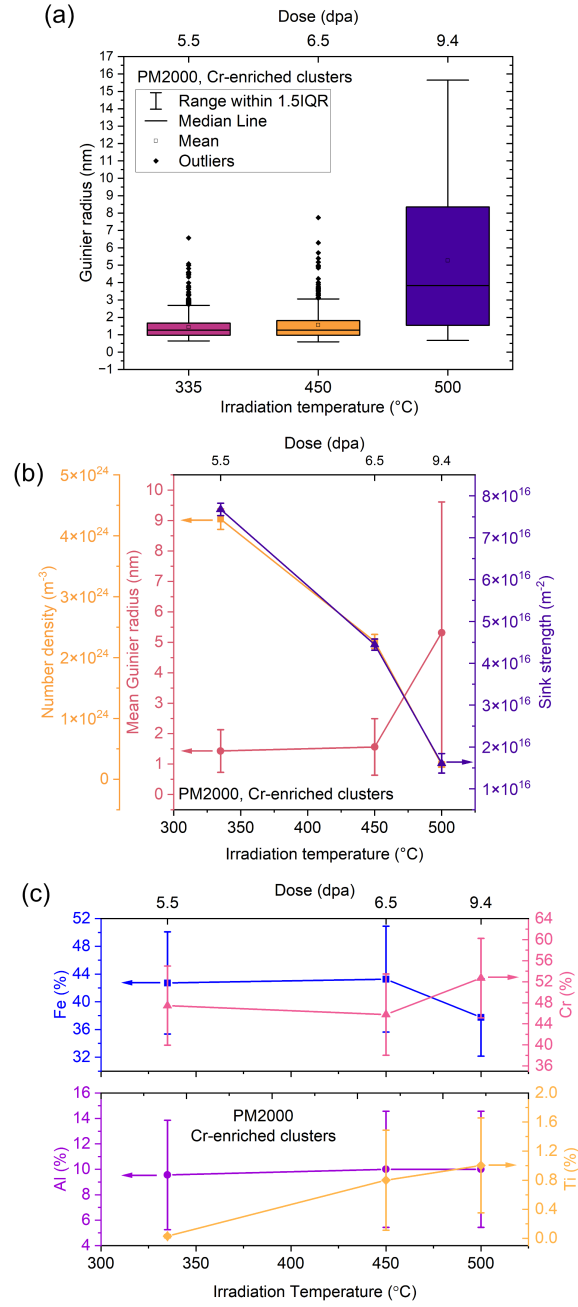


Figure 5.10: The behavior of Cr-enriched clusters in PM2000 as a function of neutron irradiation temperature. (a) The size distribution of the clusters, (b) the evolution of average size, number density, and sink strength, and (c) the evolution of cluster core composition. Atom concentrations of Fe, Cr, Al, and Ti are plotted.

Figure 5.11b. Besides the spots corresponding to the Fe-Cr-Al matrix ($a_0 = 0.287$ nm), additional diffraction spots were visible originating from a secondary phase with approximately twice the lattice parameter of bcc-Fe. The lattice parameter measured for this secondary phase was $5.79 \text{ \AA}$, and its structure appears to be cubic. A centered dark field (CDF) image using one of the extra diffraction spots is shown in Figure 5.11c. The illuminated areas correspond well with the Al-Ti-enriched areas observed by STEM-EDS.

Little evolution in solute nano-clustering was observed in PM2000 at 287°C after high-dose neutron irradiation to 55.9 dpa. Representative atom and cluster maps of Cr and Ti are shown in Figure 5.12. Similar to the 335°C , 5.5 dpa condition, no significant clustering of Al and Ti was detected. On the other hand, Cr-enriched clustering was present. The average Guinier radius of the Cr-enriched clusters was $1.5 \pm 0.7 \text{ nm}$, number density was $1.43 \pm 0.94 \times 10^{23} \text{ m}^{-3}$, and average Cr core concentration was $46.7 \pm 7.1 \text{ at.}\%$. Compared to the 335°C , 5.5 dpa condition, the Cr-enriched clusters therefore were present in lower number density, but had similar size and Cr-enrichment. However, there is a possibility that the number of Cr-enriched clusters detected in the 287°C , 55.9 dpa condition is inaccurate due to shifts in the relative abundances of isotopes at high doses. The simulated isotopic inventories calculated by FISPACT-II can be inaccurate if the thermal flux changes over the course of irradiation. While FISPACT-II calculations suggest that the Cr concentration in the sample should be 18.3 at.%, the bulk Cr concentration measured in the high-dose neutron irradiated PM2000 datasets after isotopic decomposition was $\sim 17.5 \text{ at.}\%$. By comparison, for the 335°C 5.5 dpa condition, the concentration of Cr measured by APT after isotopic decomposition was 18.2 at.% with FISPACT-II predicting 18.7 at.%. Thus, the bulk Cr concentration of PM2000 measured by APT was lower than expected at high neutron doses. For another point of reference, the bulk concentration of Cr was measured by STEM-EDS and was found to be

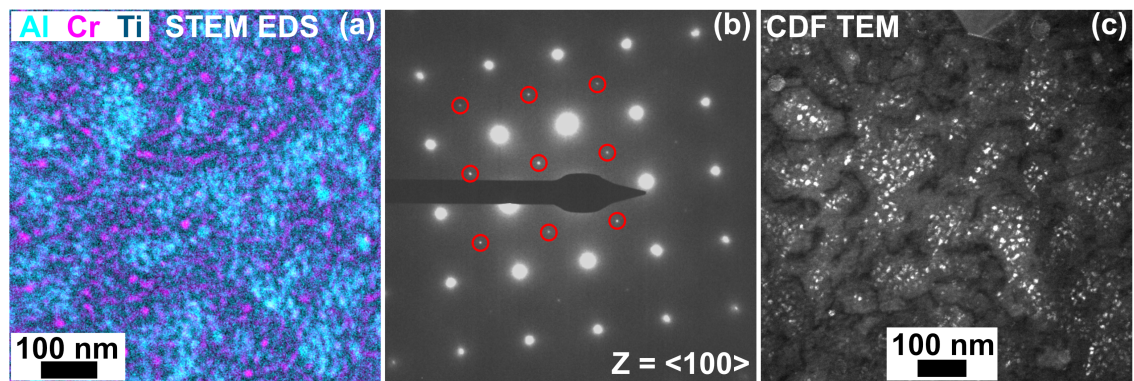


Figure 5.11: TEM analysis of PM2000 after neutron irradiation at 500 °C to 9.4 dpa. (a) A STEM-EDS map quantified by weight percent showing the distribution of Al, Cr, and Ti. (b) A selected area diffraction pattern where the matrix is oriented along the $\langle 100 \rangle$ zone axis. Superlattice diffraction spots belonging to a secondary phase are circled. (c) A CDF image formed using a superlattice reflection, showing the secondary phase precipitates are distributed in areas similar to the Al-Ti enriched regions in (a).

consistent with FISPACT-II predictions. The detection efficiency for Cr-enriched clusters by APT may be impacted by the lower bulk Cr content, since clusters were detected by the iso-position method before any composition correction was applied. Thus, the difference in Cr-enriched cluster number density observed between 5.5 and 55.9 dpa is likely to be an artifact.

Effect of temperature and dose on solute nanoclustering in MA957

After the JP-26 irradiation campaign in HFIR, MA957 samples irradiated at 335 °C, 5.1 dpa; 450 °C, 6.0 dpa; and 500 °C, 8.6 dpa were examined with APT. In addition to Y-Ti-O-rich clusters that existed in the non-irradiated microstructure, Cr, Ni, and Ti clusters were detected by comparing the local chemistry frequency distributions of actual and randomized datasets (see Figure 5.13). APT reconstructions were done with Cameca’s IVAS and the OSCAR program was used for cluster identification and analysis. The search parameters for each cluster species are provided in Table 3.9. The Ni and Ti clusters were observed to be spatially correlated. Thus, the three solute nano-clusters species characterized by APT were Cr-, Ni-Ti-, and Y-Ti-O-enriched. The Cr-, Ni-Ti-, and Y-Ti-O-enriched clusters were identified based on Cr, Ni, and TiO ions, respectively. Figure 5.14 shows representative volumes from each condition, where the solute atom maps and the associated clusters are imaged.

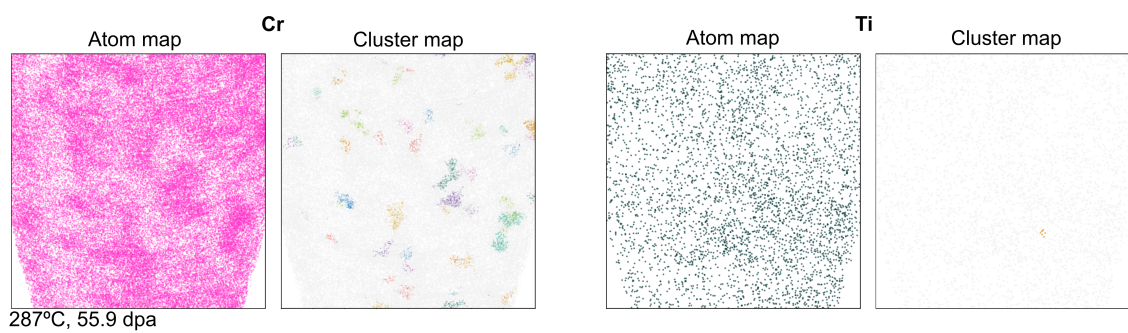


Figure 5.12: Atom and cluster maps of representative volumes from PM2000 after neutron irradiation at 287°C to 55.9 dpa

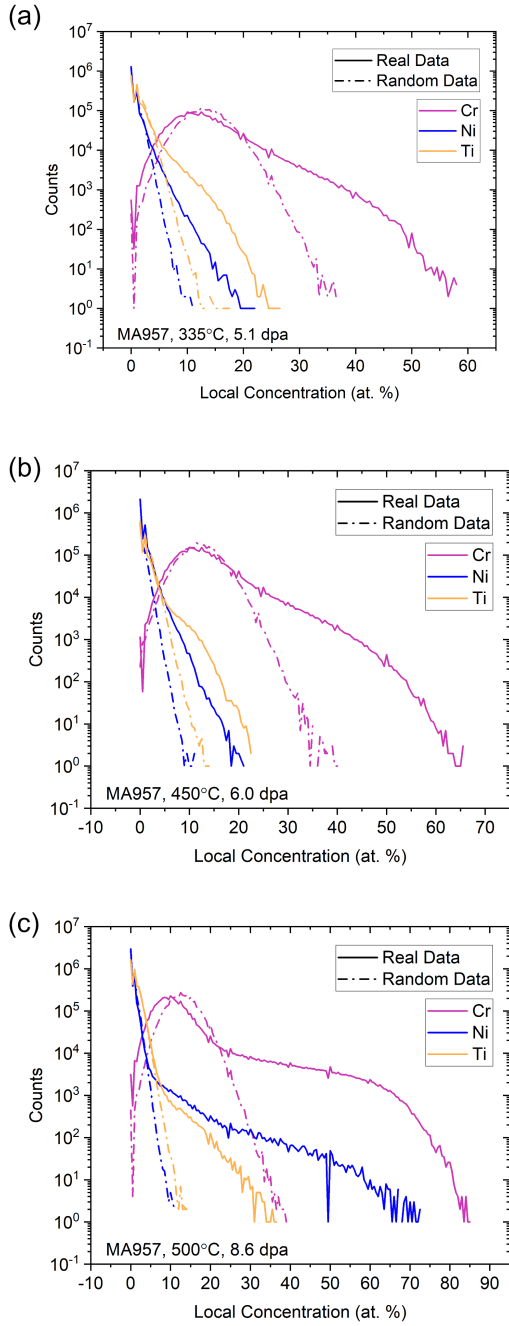


Figure 5.13: A comparison of the real and random local chemistry frequency distributions for MA957 irradiated at (a) 335 °C, 5.1 dpa, (b) 450 °C, 6.0 dpa, and (c) 500 °C, 8.6 dpa.

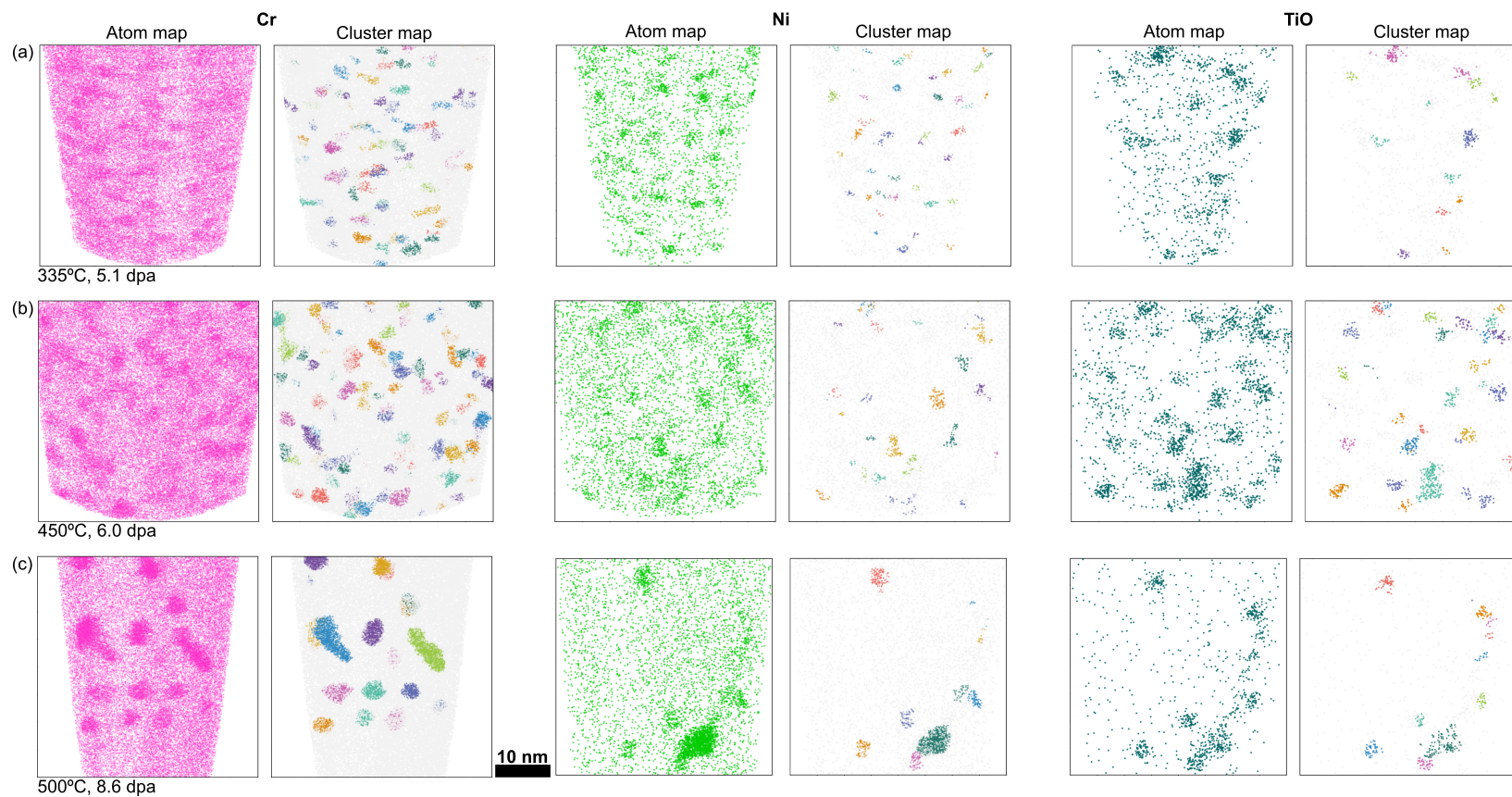


Figure 5.14: Atom and cluster maps of representative volumes from MA957 after neutron irradiation at (a) 335 °C, 5.1 dpa, (b) 450 °C, 6.0 dpa, and (c) 500 °C, 8.6 dpa. Maps for Cr, Ni, and TiO are shown. Sample volume for the Cr maps is 40 x 40 x 15 nm and 40 x 40 x 25 nm for the Ni and TiO maps.

With neutron irradiation, no significant change to the Y-Ti-O-enriched nanocluster population was observed. Figure 5.15 presents the size distributions, average Guinier radius, number density, sink strength, and core composition of the nano-oxides both initially and after irradiation. The initial microstructure of MA957 contains a high density of fine Y-Ti-O-enriched nanoclusters with an average Guinier radius and number density of 1.5 ± 0.3 nm and $6.6 \pm 0.5 \times 10^{23} \text{ m}^{-3}$, respectively, leading to a sink strength of $1.3 \times 10^{16} \text{ m}^{-2}$. Due to artifacts such as trajectory aberrations, molecular ion evaporation, and multiple hits, it is hard to accurately measure by APT the size and composition of oxides embedded in a metal matrix [242, 179, 243, 172]. Evidence of trajectory aberrations was found when measuring the atomic density across the clusters. Because the nano-oxides are low-field precipitates, the trajectory of matrix atoms are deflected inwards and there is an apparent increase in the density of hits on the detector. Figure 5.16 shows an example of the elevated atomic density measured across the oxides with a line profile. In this study, the raw composition of the oxides prior to irradiation was 64.9Fe-14.2Cr-1.5Y-9.8Ti-7.3O at.%. Such levels of Y, Ti, and O are well below those expected for $\text{Y}_2\text{Ti}_2\text{O}_7$ pyrochlores, the main species of oxide in MA957, however, they are consistent with concentrations commonly observed by APT without any data post-processing [62, 243, 242]. Since the focus here was to understand the hardening contribution of each microstructural feature, the precise chemistry of the oxides was not a primary concern. In addition, as will be discussed in detail in Chapter 6, the oxides were susceptible to ballistic mixing effects, and so compositional correction could conceal real chemical phenomena. Thus, core compositions were not corrected for APT artifacts. Oxide chemistry remained relatively constant with irradiation between 335 and 500 °C. Besides Fe and Cr, 2.4 at. % Ni was also detected in the cluster cores after irradiation at 500 °C. The presence of Ni in the oxide cores will be discussed later.

Changes in the average Guinier radius of the TiO-enriched clusters, plotted in Figure 5.15b, were within error, although the average Guinier radius did appear

to increase slightly with irradiation temperature. Given local magnification effects from trajectory aberrations, it is possible that the measured Guinier radii are overestimated. The majority of the oxides had a shape factor greater than 1, where shape factor is defined in Ref. [172] as $S = XY/Z^2$. Thus, the oxides tended to appear expanded in the plane normal to the evaporation direction (the X-Y direction). However, because no widely accepted method exists for correcting the cluster radii, the values reported here are again uncorrected. As can be seen in Figure 5.15b, there was notable variation in the number density of TiO-enriched clusters observed in the non-irradiated alloy and at each irradiation temperature. This was consistent with the known heterogeneous spatial distribution of oxides in MA957.

Increasing irradiation temperature appeared to have a coarsening effect on the Cr-enrich clusters that formed. As can be seen in Figure 5.17a, the Guinier radii of the clusters increased with irradiation temperature between 335 and 500 °C. While the size of the clusters increased with temperature, their number density declined (see Figure 5.17b). As a result, sink strength of the Cr-enriched clusters was less at 500 °C than at the lower irradiation temperatures. Despite a decrease in number density, the volume fraction of clusters increased from 3.5 to 8.1 % and the percentage of Cr atoms in clusters rose from 6.6 to 21.1 % as irradiation temperature increased from 335 to 500 °C. The high fraction of Cr atoms partitioned into clusters at 500 °C was reflected by cluster enrichment. After neutron irradiation at 335 °C there was approximately 47 at.% Cr in the clusters. The core Cr concentration of the clusters increased to ~ 62 at.% at 500 °C. Based on the average proxigram measured near the interface of Cr-rich clusters, the average concentration of Cr in the matrix was approximately 13.4, 12.6, and 11.7 at. % for the 335, 450, and 500 °C conditions, respectively.

Ni-Ti-enriched clusters were present in a much lower volume fraction (< 1.5 %) compared to the Cr-enriched clusters. However, the overall behavior of the Ni-Ti-enriched clusters was qualitatively similar to the Cr-enriched clusters: as irradiation temperature increased, the size of the clusters increased, and so too did the volume

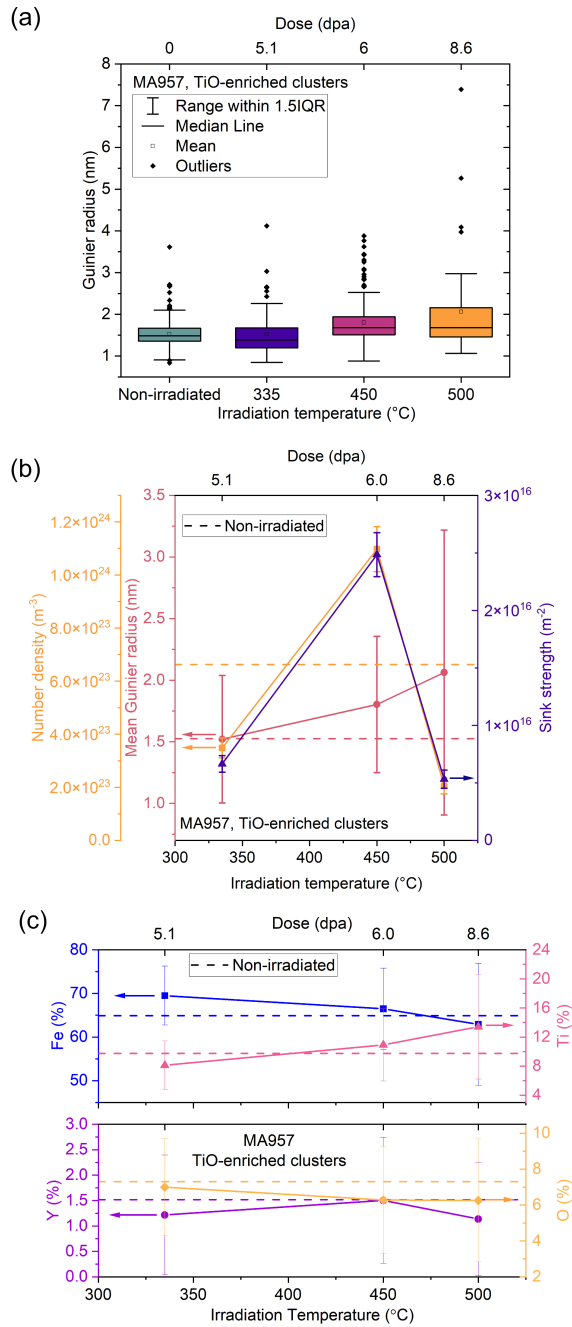


Figure 5.15: Characterization of the non-irradiated TiO-enriched clusters in MA957 and their behavior as a function of neutron irradiation temperature. (a) The size distribution of the clusters, (b) the evolution of average size, number density, and sink strength, and (c) the evolution of cluster core composition. Atom concentrations of Fe, Y, Ti, and O are plotted. Non-irradiated values in (b) and (c) are indicated by the dashed lines.

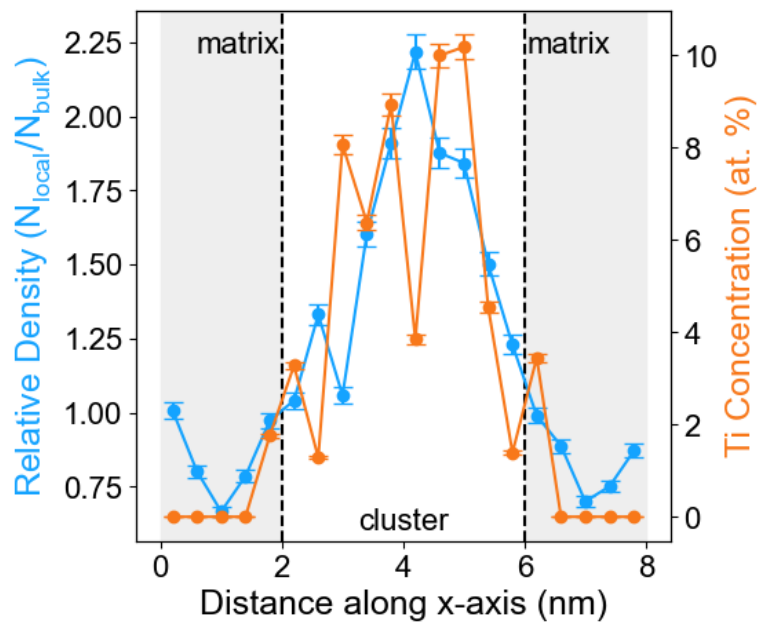


Figure 5.16: A line profile of relative density and Ti concentration across an oxide nanocluster. A cylindrical probe 0.75 times the cluster radius was used for measurement. Each measurement slice was 0.4 nm thick.

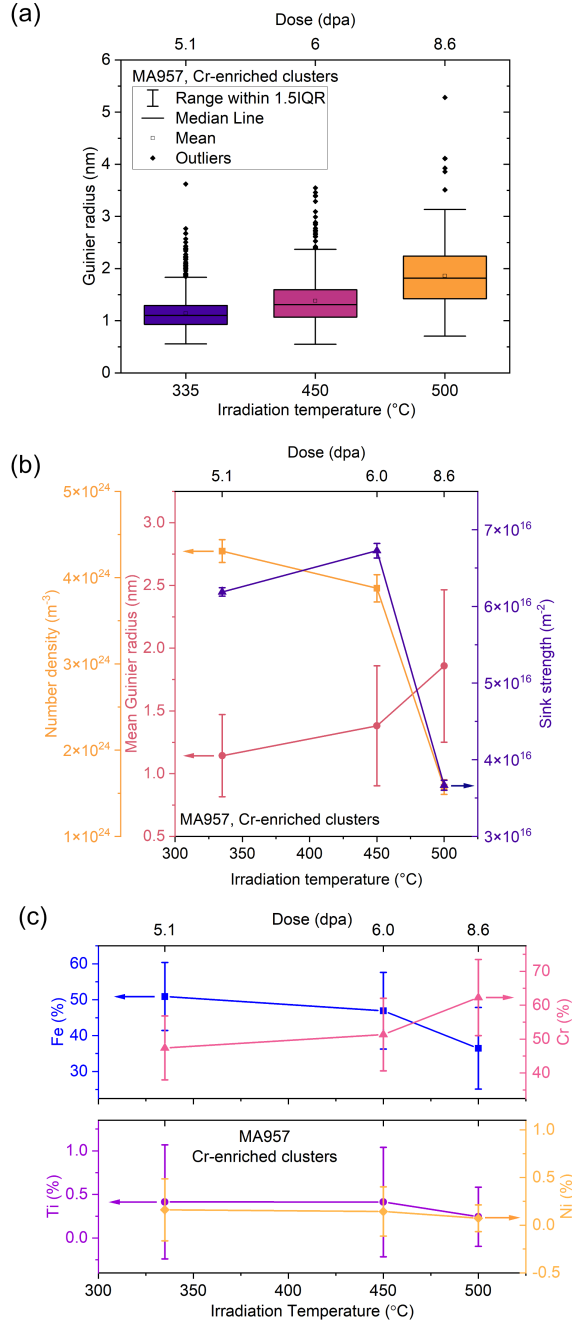


Figure 5.17: The behavior of Cr-enriched clusters in MA957 as a function of neutron irradiation temperature. (a) The size distribution of the clusters, (b) the evolution of average size, number density, and sink strength, and (c) the evolution of cluster core composition. Atom concentrations of Fe, Cr, Ti, and Ni are plotted.

fraction of clusters. Quantitative results are presented in Figure 5.18. At each irradiation condition, the average Guinier radius of the Ni-Ti-enriched clusters was nearly identical to the Cr-enriched ones. However, their number density was close to an order of magnitude lower. Interestingly, there appeared to be a spatial correlation between the Ni-Ti-enriched and Y-Ti-O-enriched nanoclusters at 450 and 500 °C, which is visually captured in Figure 5.14. At 500 °C, the association is almost one to one. Between 335 and 500 °C, there was an increase in number density observed (see Figure 5.18b), which seems to oppose the trend of coarsening with irradiation temperature. However, this uptick in number density corresponds well with the increased number of Y-Ti-O-enriched clusters observed at 450 °C. The Ni content of the clusters, given in Fig. 5.18c, remained relatively constant, around 7.6 at. %, at all irradiation temperatures. Between 335 and 450 °C, Ti content was also stagnated (~ 6.2 at. %), however, after neutron irradiation at 500 °C, the clusters contained nearly twice the amount of Ti. Also, at this irradiation temperature, approximately 3.3 at.% oxygen was detected in the Ni-Ti-enriched clusters. On the other hand, chromium content was below matrix levels in the cluster cores at all irradiation temperatures, averaging ~ 8 at. %, which suggests the Ni-Ti-enriched clusters may be anti-correlated to the Cr-enriched clusters.

To better understand the relationship between the Ni-enriched and TiO-enriched clusters, STEM-EDS maps were collected from the 500 °C irradiation condition. Figure 5.19 presents spectral images quantified by weight percent, showing the distribution of Y, Ti, and Ni. It can be seen that Ni and Ti segregate at the interface of the oxides, and well-defined Ni-Ti-enriched clusters tend to heterogeneously nucleate at the corner of the oxides. Unlike what the APT data suggests, Ni does not appear concentrated inside the oxides. While the oxides analyzed with STEM-EDS were larger than the Y-Ti-O-enriched clusters detected by APT, RIS behavior is expected to be similar. Thus, it is likely that the Ni and O measured inside the Y-Ti-O- and Ni-Ti-enriched clusters, respectively, by APT are merely the result of trajectory aberrations.

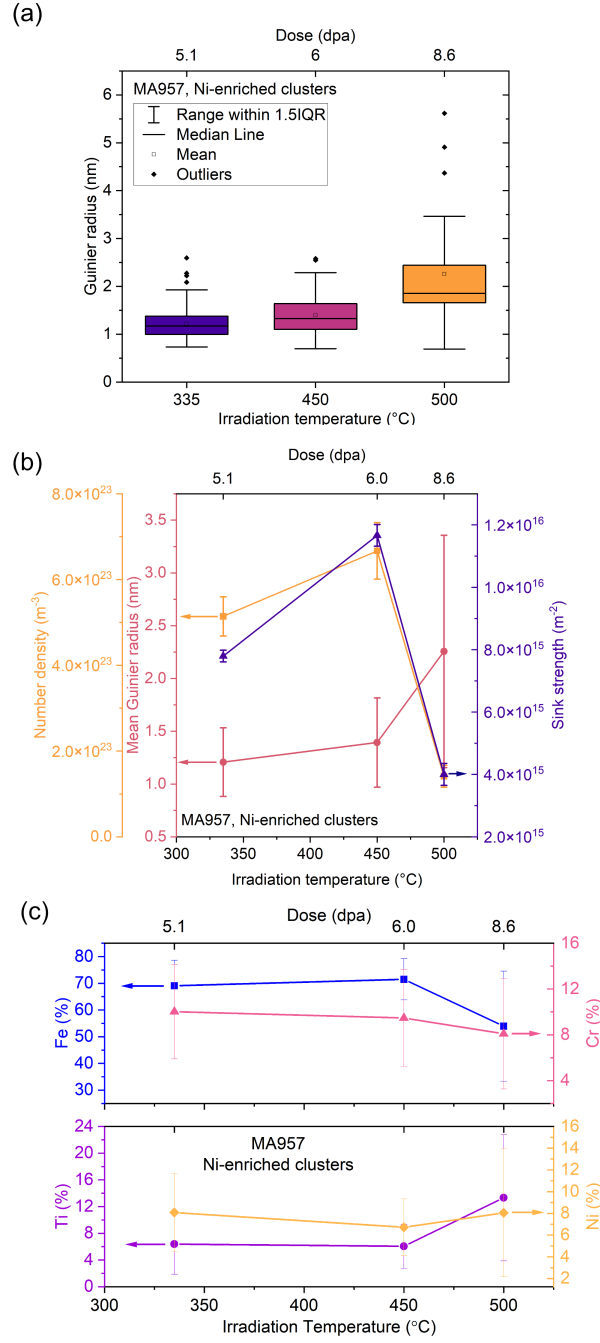


Figure 5.18: The behavior of Ni-enriched clusters in MA957 as a function of neutron irradiation temperature. (a) The size distribution of the clusters, (b) the evolution of average size, number density, and sink strength, and (c) the evolution of cluster core composition. Atom concentrations of Fe, Cr, Ti, and Ni are plotted.

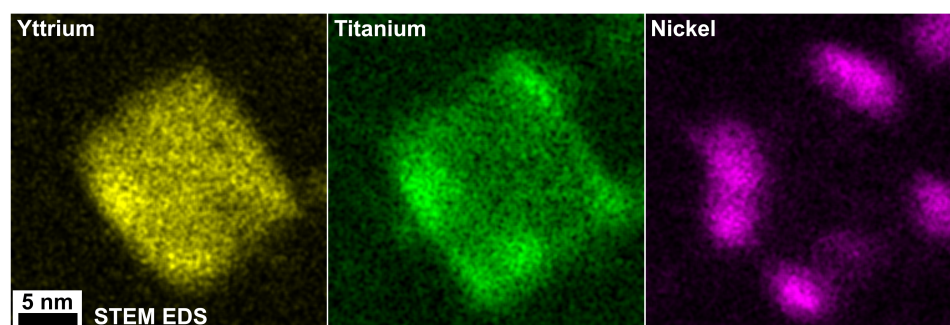


Figure 5.19: STEM EDS spectral images of a nano-oxide in MA957 irradiated at 500 °C to 8.6 dpa. Maps for Y, Ti, and Ni and quantified according to weight percent.

Solute nanoclustering in the MA957 sample irradiated at 287 °C to 51.5 dpa was also examined by APT. Cr-enriched and Y-Ti-O-enriched clusters were identified using the same methodology and search parameters as for the low dose samples. Solute atom maps and associated clusters identified for needles sampled from each condition are given in Figure 5.20.

It is important to note that Ni-Ti-enriched clustering was present in MA957 after neutron irradiation at 287 °C to 51.5 dpa. This was verified by STEM-EDS spectral mapping (see Figure 5.21). However, due to issues with the isotopic decomposition, the Ni-Ti enriched clusters could not be accurately characterized by APT for this high dose condition. Without isotopic decomposition, ~ 2.1 at.% Ni was detected in the APT volumes. However, the nominal concentration of Ni in MA957 is 0.30 at.%, and this was confirmed by STEM-EDS. The high concentration of Ni in the APT datasets arises from the 29 Da peak in the mass-to-charge ratio spectrum. Both Ni-58 and Fe-58 share the 29 Da peak, and so isotopic decomposition is needed to resolve this overlap. Unfortunately, when isotopic decomposition of the bulk concentration was performed, the output indicated no Ni was present. The inability to successfully resolve the overlap at 29 Da suggests that the thermal spectrum supplied into FISPACT-II to calculate isotopic inventories may not be accurate for such high doses. By contrast, for the irradiation doses between 5.1 and 8.6 dpa, the overlap between Ni-58 and Fe-58 was deconvolved based on the relative isotopic abundances calculated with FISPACT-II.

For the Cr-enriched clusters, average Guinier radius was larger (1.7 ± 0.5 nm vs 1.1 ± 0.3 nm) and number density was lower ($2.6 \pm 0.1 \times 10^{24} \text{ m}^{-3}$ vs $4.3 \pm 0.1 \times 10^{24} \text{ m}^{-3}$) than after irradiation at 335 °C to 5.1 dpa. In addition, ~ 24 % of Cr atoms were partitioned in clusters at 51.5 dpa compared to only ~ 5 % at 5.1 dpa. Cr content in the cluster cores also increased by ~ 11 at. %. These trends suggest coarsening of the Cr-enriched clusters with irradiation dose. On the other hand, no significant changes compared to the 5.1 dpa condition were noted to the Y-Ti-O-enriched clusters.

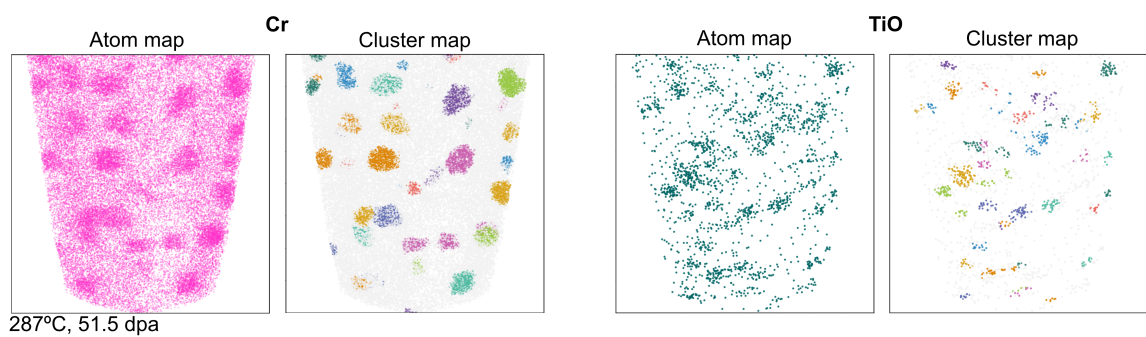


Figure 5.20: Atom and cluster maps of representative volumes from MA957 after neutron irradiation at 287 °C to 51.5 dpa. Maps for Cr and TiO are provided.

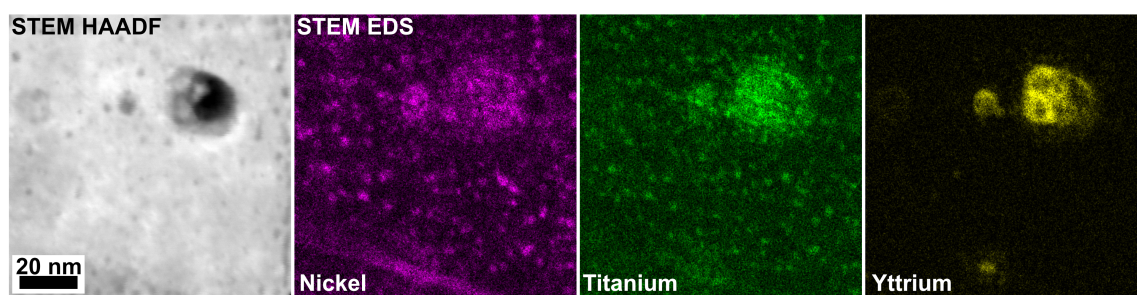


Figure 5.21: STEM HAADF and EDS of MA957 after irradiation at 287 °C to 51.5 dpa. The area imaged contains a couple of heavily damage oxides (see Chapter 6) as well as Ni and Ti clustering throughout the matrix. All STEM EDS maps are quantified by weight percent.

5.1.3 Other microstructural features contributing to hardening in irradiated MA957

The non-irradiated grain size in this heat of MA957 has been measured in previous studies with electron backscatter diffraction as $\sim 630 - 800$ nm (in the transverse direction, normal to the tube length) [160, 244]. With irradiation between 335 and 500 °C, no grain growth is expected.

Network dislocation density, ρ_d , was measured from BF STEM images using the line-intercept method:

$$\rho_d = \frac{2n}{lt} \quad (5.1)$$

where n is the number of intercepts, l , is the line length, and t is the thickness of the TEM foil. At least five lines oriented randomly were used for each image. The dislocation line density measured in the non-irradiated MA957 was $2.1 \pm 0.5 \times 10^{14} \text{ m}^{-2}$. This value is slightly lower than reported in Ref. [244], where the same heat of MA957 was also examined. Given heterogeneities in the microstructure, a reasonable estimate of the initial dislocation density is therefore $\sim 5.2 \times 10^{14} \text{ m}^{-2}$. Under irradiation at 335 to 500 °C with doses between 5.1 and 8.6 dpa, there was no significant change to dislocation density.

In bcc-Fe steels, both $1/2 < 111 >$ and sessile $< 100 >$ loops can develop under irradiation [245]. Figure 5.22 shows BF STEM images compiled from each low dose irradiation condition. Imaging was done with a two-beam condition. In general, the dislocation microstructures were dominated by network rather than loop dislocations. Loop densities of $1.1 \pm 0.3 \times 10^{21}$, $7.5 \pm 1.9 \times 10^{20}$, and $8.2 \pm 2.1 \times 10^{20} \text{ m}^{-3}$ were measured for the samples irradiated at 335, 450, and 500 °C, respectively. While dislocation loops should readily form in ferritic alloys under neutron irradiation at 335 °C, a high initial dislocation density may have suppressed loop nucleation [246]. At 500 °C, loops also form, but grow rapidly and merge with the dislocation network.

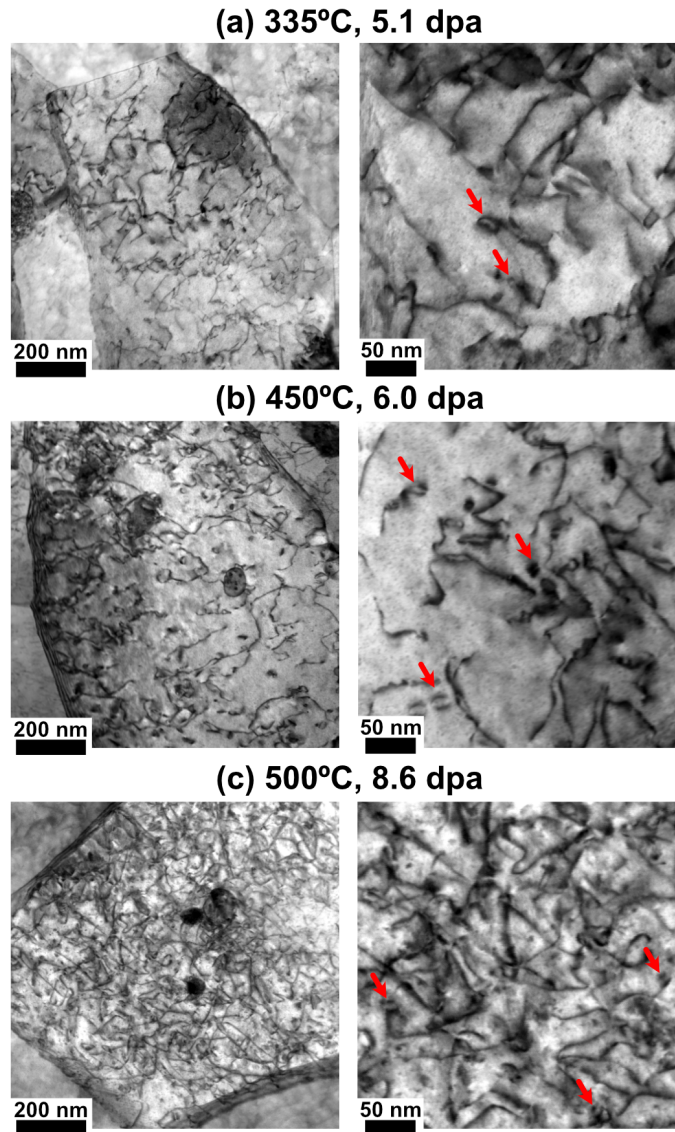


Figure 5.22: BF STEM images of the dislocation microstructure in MA957 after neutron irradiation at (a) 335 °C, 5.1 dpa, (b) 450 °C, 6.0 dpa, and (c) 500 °C, 8.6 dpa. Dislocation loops are indicated with red arrows.

Thus, the low density of dislocation loops observed in irradiated MA957 follows the trends of expected dislocation behavior for ferritic steels.

5.2 Discussion

5.2.1 Quantifying the contribution of microstructural features to hardening in MA957

Unlike RAFM steels that typically show minimal hardening after irradiation at $> 400^\circ\text{C}$, all three of the ODS alloys examined by post-irradiation mechanical testing retained some degree of hardening. To understand the origin of this radiation-induced hardening in MA957, yield strength measurements from the uniaxial tensile tests were compared to the calculated yield strength for the low dose ($5.1 - 8.6$ dpa) 335, 450, and 500°C irradiations.

The hardening contributions of grain boundaries, dislocation lines, dislocation loops, lattice friction (Peierls-Nabarro) stress, Cr solute strengthening, nano-oxides, Cr-enriched clusters, and Ni-enriched clusters were considered in modelling yield strength. Grain boundaries, dislocations lines, and dislocation loops were deemed strong obstacles to dislocation glide with barrier strengths, α , greater than 0.25. On the other hand, the remaining components of the microstructure were treated as weak barriers with $\alpha \leq 0.25$. Barriers of similar strength were combined by root-sum squared superposition, and then the hardening contributions from both strong and weak barriers were summed. Yield strength, σ_{YS} , was therefore calculated by:

$$\sigma_{YS} = \sqrt{\sigma_{gb}^2 + \sigma_{line}^2 + \sigma_{loop}^2} + \sqrt{\sigma_{PN}^2 + \sigma_{ss}^2 + \sigma_{no}^2 + \sigma_{Crc}^2 + \sigma_{Nic}^2} \quad (5.2)$$

where the subscripts *gb*, *line*, *loop*, *PN*, *ss*, *no*, *Crc*, and *Nic* refer to grain boundaries, dislocation lines, dislocation loops, Pierels-Nabarro stress, solute strengthening, nano-oxides, Cr-enriched clusters, and Ni-enriched clusters, respectively.

Glissile $a/2 < 111 >$ edge dislocations are expected to be the dislocation type that interacts with the barriers in bcc-Fe systems. Thus, a Burgers vector, b , of 0.249 nm ($a = 0.287$ nm) was used throughout the calculations. In addition, the shear modulus, μ , of MA957 was estimated to be ~ 81 GPa at room temperature [247]. Finally, the Taylor factor, M , was needed to relate critically resolved shear stress to yield stress. In equiaxed polycrystalline bcc metals, M is close to 3.06 [57].

Grain boundary strengthening was calculated using the Hall-Petch relationship:

$$\sigma_{gb} = \frac{k}{\sqrt{d}} \quad (5.3)$$

where k is the strengthening coefficient and d is grain diameter. A value of $338 \text{ MPa}\sqrt{\text{m}}$, which was previously determined for ODS alloy 14YWT based on tensile tests at room temperature, was used for k [247]. The grain diameter that was measured in Ref. [160] for the non-irradiated condition was assumed to be unchanged after neutron irradiations between 335 and 500 °C.

In the matrix, the intrinsic friction force that opposes dislocation glide in the absence of thermal activation is known as the Peirels-Nabarro stress. It varies as the dislocation glides over a periodic array of atoms, however the critical stress required for movement is given by [248]:

$$\sigma_{PN} = \frac{2M\mu}{1-\nu} \exp \left[\frac{-2\pi a}{b(1-\nu)} \right] \quad (5.4)$$

where ν is Poisson's ratio (~ 0.3). The addition of Cr to the bcc-Fe matrix also results in hardening. Zhu et al. found that solute solution strengthening in Fe-Cr binary alloys can be well modelled by the relationship [249]:

$$\sigma_{ss} = 40.71c^{2/3} - 134.76 \quad (5.5)$$

where c is Cr concentration in weight percent. Based on the APT results, Cr content in the matrix was estimated as 13.4, 12.6, and 11.7 wt.% for the 335, 450, and 500 °C irradiations, respectively.

Forest hardening was used to describe strengthening from line dislocations. Change in yield strength was calculated based on dislocation density, ρ_d by:

$$\sigma_{line} = M\alpha\mu b\sqrt{\rho_d} \quad (5.6)$$

Orowan hardening from an array of barriers follows a similar form. Seeger developed the dispersed barrier hardening (DBH) model [56] to estimate the strengthening of barriers with diameter d and number density N :

$$\sigma = M\alpha\mu b\sqrt{Nd} \quad (5.7)$$

However, for weak obstacles, dislocations interactions are less localized and tend to involve lower bowing angles. A more appropriate description of the hardening for weak barriers is therefore given by the Friedel–Kroupa–Hirsch (FKH) model, which considers force to be distributed uniformly along the length of the dislocation line [60, 61]:

$$\sigma = M\alpha\mu bdN^{2/3} \quad (5.8)$$

Knowledge of barrier strengths is a key limitation to the application of Equations 5.6 – 5.8. For polycrystalline Fe, literature suggests the barrier strength of dislocation lines is 0.38 [247]. Bergner et al. found barrier strengths of 0.048 ± 0.012 for α' precipitates and 0.40 ± 0.16 for dislocation loops in neutron-irradiated Fe-Cr alloys using several different hardness models [250]. Similarly low barrier strengths, between 0.04 and 0.08, were calculated for α' for the DBH model by Zhu et al. [249] depending on size, using the method outlined in Ref. [59]. However, barrier strengths were found to increase to 0.07 – 0.24 for particles in the range of 2 – 7 nm with the FKH model.

A relationship between barrier strength and particle radius, r , was also proposed by Alinger for nano-oxides based on fitting of experimental data from nanostructured ferritic alloys [251]:

$$\alpha(r) = -0.017 + 0.347 \log(r/2b) \quad (5.9)$$

Using this equation, the barrier strength for the nano-oxides in MA957 is expected to be between 0.16 and 0.21. To avoid convolution of the model with the local variations in oxide density seen in the APT results, average size and density measured across all the conditions were used to calculate the oxide hardening contribution by Equations 5.8 and 5.9. This is considered a reasonable assumption because the size and density of the oxides did not systematically vary with irradiation temperature.

To our knowledge, no barrier strength information exists specifically on Ni-Ti-enriched clusters in ferritic alloys. For Ni-Si-P-Cr-enriched clusters in Fe-12Cr, Bergner et al. calculated a barrier strength of 0.27 ± 0.06 , suggesting that Ni-enriched clusters may potentially act as strong barriers [250]. However, given the low enrichment levels of Ni and Ti detected by APT in the cluster cores (~ 7.4 at.% Ni and ~ 6.2 at.% Ti) after neutron irradiation at 335 and 450 °C, the clusters were treated as weak barriers, assuming $\alpha = 0.1$. For the 500 °C irradiation condition, Ni-enriched clusters were excluded from the hardness analysis, since our TEM results suggest the Ni-enriched clusters are attached to the nano-oxide interfaces rather than disperse in the matrix. A full list of the barrier strengths used for calculations are provided in Table 5.2.

When the Cr-enriched clusters had a barrier strength of 0.14, relatively good agreement between the yield strengths measured by uniaxial tensile tests and calculated using the hardness model of Equation 5.2 was achieved, as can be seen in Figure 5.23. For each neutron irradiation condition, the relative contribution from each microstructural feature to hardening is also depicted graphically. Grain boundaries and network dislocations were responsible for nearly half of the alloy's

Table 5.2: Barrier strengths of microstructure features in MA957

Feature	α
dislocation lines	0.38
dislocation loop	0.4
nano-oxides	0.19
Cr-enriched clusters	0.14
Ni-enriched clusters	0.1

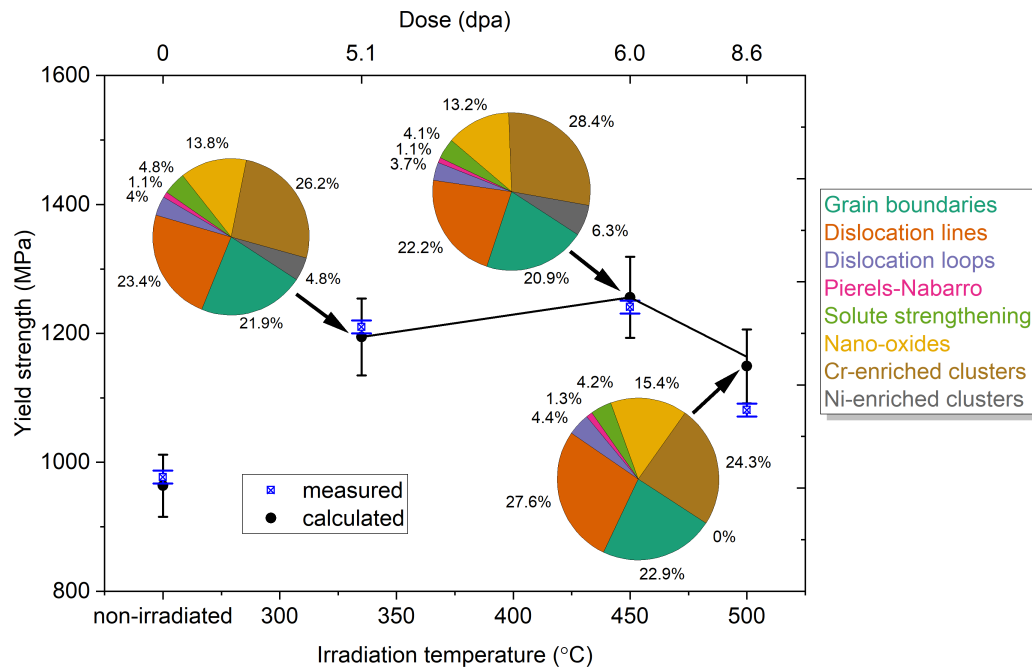


Figure 5.23: A comparison of yield strength in neutron irradiated MA957 as measured by uniaxial tensile tests and calculated using the hardness model in Equation 5.2. The relative contribution from each microstructural feature is shown in the inset pie charts.

strength. However, as these features varied little under irradiation, they did not account for the retained hardness seen in MA957 at irradiation temperatures $\geq 450^\circ\text{C}$. Rather, Cr-enriched clusters contributed more than 24 % to the total strengthening under irradiation. Despite the coarsening of the Cr-enriched clusters at 500°C , the contribution of the clusters remained relatively constant with irradiation temperature. At 500°C , the model overestimates the measured yield strength, although the calculated value is nearly within error. This discrepancy may exist because Fe has a lower shear modulus than Cr, and so with a high fraction of Cr ($\sim 21\%$) in clusters after irradiation at 500°C , the shear modulus of the matrix may be lower than in the non-irradiated case.

The barrier strength of 0.14 for Cr-enriched clusters that provided good agreement with the mechanical testing results falls into the range of values reported by others for α' using the FKH model [249]. However, considering the enrichment levels in the cluster cores detected by APT ($\sim 47 - 62\text{ at.}\%$), it is perhaps surprising that the barrier strength was so high. It is possible, that the hardening contribution of the Ni-enriched clusters is underestimated by a barrier strength of 0.1.

Mechanical testing data presented in Figures 5.2 and 5.4 suggests that additional hardening can occur in MA957 at higher doses ($> 6\text{ dpa}$) for irradiation temperatures $\leq 450^\circ\text{C}$. The coarsening of Cr-enriched clusters with dose that was observed by APT may explain this. Alternatively, if the barrier strength of the Ni-enriched clusters is in reality higher than 0.1, it could also be a concern for the high dose operation of MA957 at or below 450°C . STEM-EDS maps from MA957 after neutron irradiation at 287°C to 51.5 dpa suggests that Ni-enriched clustering also may not saturate by 5 dpa given that at 51.5 dpa, the Ni clustering appeared quite pervasive. Unfortunately, due to complications with isotopic decomposition at high neutron irradiation doses, the Ni-enriched clusters could not be precisely characterized by APT.

5.2.2 Radiation enhanced, induced, and modified precipitation in neutron irradiated ODS alloys

In the neutron irradiated PM2000 and MA957 samples, Cr-enriched clusters were detected at all irradiation temperatures up to 500 °C. Radiation-enhanced precipitation of the Cr-rich α' phase is to be expected in Fe-Cr based ODS alloys when Cr content exceeds the solubility limit [39]. However, this solubility limit under irradiation is poorly understood, even for the Fe-Cr binary system. At 335, 450, and 500 °C, calculations by Xiong et al. suggest a Cr solubility limit of ~ 10 , 12.5, and 14.5 at.%, respectively [5]. Experimentally, Novy et al. found with thermal aging the Cr solubility limit was 14 at.% at 500 °C [252]. The observation of a high volume fraction (8.1 %) of Cr-enriched clusters in MA957 after irradiation at 500 °C also indicates a solubility limit less than 15.15 at.% Cr (14.34 wt. % Cr). Another variant of MA957 with slightly lower Cr content (13.8 wt. %) was examined in Refs. [136] and [253]. After neutron irradiation of MA957 in the FFTF to 109 – 113 dpa, Bailey et al. observed Cr-enriched clusters at 412 °C, but not at 550 and 670 °C [136]. Wang et al. also observed the nucleation of Cr-enriched clusters up to 450 °C using ion irradiations with significantly faster damage rates, where ballistic dissolution is more likely to disruption precipitation than during neutron irradiation [253]. Thus, considering all the experimental data, the conservative estimate remains that the Cr solubility limit at ~ 500 °C under irradiation is ~ 14 at.%.

Assuming the MA957 examined in this study has a bulk Cr concentration greater than the solubility limit, it is surprising that the clusters had Cr enrichment levels well below those expected at thermal equilibrium (47 – 62 at.% after neutron irradiation vs ~ 80 – 90 at.% at thermal equilibrium). It is possible that minor solute elements found in ferritic ODS alloys are influencing the kinetics or thermodynamic driving force for α' formation. As Cr content in the cluster cores was still below thermal equilibrium levels at > 50 dpa, it seems more likely that thermodynamics and not

kinetics are impeding alpha prime formation. The Cr core concentrations of Cr-enriched clusters were similarly low in neutron-irradiated PM2000, which assuredly has a bulk Cr content greater than the solubility limit at 500 °C. For Fe-Cr-Al alloys like PM2000, several studies have found a correlation between aluminum content and α' precipitation [254, 255, 256]. Based on modeling, aluminum is suspected of increasing the formation energy of α' by causing local magnetic frustrations [257]. A similar suppression effect may be occurring in MA957. Calculations suggest molybdenum may reduce the temperature range over which α' precipitation occurs, while nickel additions can decrease the mass fraction [258]. However, considering the low concentrations of Mo and Ni in MA957, it is unclear whether these solute elements have a significant effect on Fe-Cr phase separation. In particular, during irradiation at 500 °C, Ni is segregated at the oxide interfaces and at grain boundaries and therefore may not affect phase stability in the matrix.

In addition to Cr-enriched clusters, Ti-enriched ones were observed in both MA957 and PM2000 after neutron irradiation at 500 °C. In MA957, the Ti partitioned with Ni while in PM2000, it was with Al. Below 500 °C, Ni-Ti-enriched clusters were in lower volume fraction in MA957, and Al-Ti-enriched clusters in PM2000 were non-existent. It thus appears that the migration of Ti in Fe-based alloys becomes substantial under neutron irradiation between 450 and 500 °C. Unfortunately, there are limited modelling results that shed insight on the radiation enhanced diffusion of Ti in Fe-based alloys. A rate theory model by Nellis and Hin for grain boundary RIS in Fe-Y-Ti-O alloys predicts Ti enrichment up to 527 – 627 °C [259]. At higher temperatures, segregation appears to be dominated by a vacancy mechanism, which allows titanium to migrate away from the grain boundaries faster than it is supplied by the interstitial dumbbells. Additional neutron irradiation data above 500 °C would be useful to confirm the peak RIS temperature for Ti. RIS of Ni and Ti to the nano-oxide interfaces at 500 °C likely produces the radiation-induced clusters observed in MA957.

The Al-Ti-enriched phase that forms in neutron-irradiated PM2000 at 500 °C may be radiation-modified or retarded. During thermal aging experiments of PM2000 at 435 °C, Capdevila et al. reported precipitation of a β' phase consisting of 49Fe-25Al-15Ti-11Cr at.% [260]. The interplanar distances measured by HRTEM in their work were consistent with a Fe₂AlTi L21 structure, which has a lattice parameter of 0.588 nm. A similar lattice parameter of 0.579 nm was measured from the selected area diffraction patterns collected after irradiation at 500 °C to 9.4 dpa (see Figure 5.19). However, the composition of the phase was different than reported by Capdevila et al. Here, the Al-Ti-enriched phase consisted of 47Fe-18Al-7Ti-27Cr at.%. Thus, the clusters that formed under irradiation contained substantially more Cr and less Al and Ti. Jung et al. also observed precipitation of an Al-Ti-enriched phase in PM2000 after neutron irradiation in HFIR to ~ 21 dpa at 500 °C [141]. They measured a lattice parameter of 0.574 nm, and hypothesized that the phase was Fe₃Al with D03 structure. Similar to our results, the chemistry of the phase Jung et al. encountered, 55Fe-20Al-5Ti-20Cr at.%, was higher in Cr and lower in Al and Ti than β' . Given the minimal difference with our results, the composition of the Al-Ti-enriched phase appears to reach steady-state by 9.4 dpa after neutron irradiation at 500

5.3 Conclusions

Vickers microhardness and uniaxial tensile tests were performed on samples of 12YWT, MA957, and PM2000 that were neutron-irradiated in HFIR between 335 and 500 °C with doses ranging between 5 and 13.1 dpa. A loss of uniform and total elongations with irradiation dose was observed, although in the case of MA957 there was still considerable uniform elongation up to 13.1 dpa. More surprisingly, the ODS alloys appeared to show hardening for irradiation temperatures ≥ 450 °C, at which RAFM steels would normally recover or soften. This observation seems to contradict the idea that high sink strengths materials can mitigate radiation hardening and embrittlement.

To understand the underlying cause of this phenomenon, the irradiated microstructures of MA957 and PM2000 were examined by TEM and APT. In neutron-irradiated PM2000, a high volume fraction of Cr-enriched clusters were observed at each irradiation condition. These Cr-enriched clusters are likely to be nucleating α' precipitates, since their core concentrations were well below values expected α' at thermal equilibrium. In addition, an Al-Ti-enrich phase precipitated after irradiation at 500 °C. Considering reports of β' observed in PM2000 after thermal aging at 435 °C, this phase appears to be radiation modified or retarded.

In MA957, Cr-enriched clustering also occurred under irradiation at 287 – 500 °C. Unlike with PM2000, the clusters appeared to coarsen to some degree with dose. Ni-Ti-enriched clusters were also observed at each irradiation temperature. After neutron irradiation at 500 °C to 8.6 dpa, the Ni-Ti-enriched clusters appeared to be directly associated with the Y-Ti-nano-oxides. The Ni-Ti-enriched clusters are therefore likely radiation-induced by solute-point defect flux couplings.

Using size, density, and chemistry information measured by APT for the solute nanoclusters, radiation hardening was modelled in MA957. The model used included contributions from grain boundaries, dislocation lines, dislocation loops, lattice friction (Peierls-Nabarro) stress, Cr solute strengthening, nano-oxides, Cr-enriched clusters, and Ni-enriched clusters. With reasonable barrier strength values for the Cr-enriched clusters, the model was able to explain the hardening measured during uniaxial tensile tests. While grain boundaries and network dislocations were key contributors to non-irradiated strength, the Cr-enriched clusters were mainly responsible for radiation induced hardening. Compared to RAFM steels, radiation induced hardening may have even greater consequence in ODS alloys because of their poor initial fracture toughness. The results highlight that the proposed range of operating temperatures for high Cr-ODS alloys may be limited by their susceptibility to radiation-enhanced Cr-enriched clustering.

Chapter 6

Stability of oxides after high dose neutron irradiation

In literature, there is no consensus on a fundamental point: whether oxides in ODS steels are stable under neutron irradiation. Especially for advanced reactor concepts, ODS alloy will need to withstand lifetime doses of at least 50 dpa. The structural and chemical evolution of oxides up to 50 dpa was therefore investigated in neutron-irradiated PM2000 and MA957.

6.1 Results

6.1.1 Instability of YAP nanodispersoids in PM2000

Chemistry and structure of nanodispersoids prior to irradiation

As the structure and chemistry of nanodispersoids in ODS alloys can vary, we characterized the oxides in PM2000 prior to irradiation with scanning TEM (STEM), high throughput energy dispersive X-ray spectroscopy (EDS), and atomic resolution STEM. Figure 6.1a shows a portion of the microstructure imaged in high-angle annular dark field (HAADF). With this imaging technique, brightness scales with the atomic number of the elements. The nanodispersoids were observed to

be homogeneously distributed throughout the microstructure. The average Feret diameter of the nanodispersoids was 25.1 ± 1.0 nm and density of the nanodispersoids was $8.26 \pm 1.23 \times 10^{20} \text{ m}^{-3}$.

In Figure 6.1c, EDS maps of the area imaged in HAADF are given. In addition, an example EDS line scan of a nanodispersoid is given in Figure 6.1b with the concentrations of Fe, Cr, Y, Al, and Ti provided. It is important to note that because O cannot be well-quantified by EDS, O is not plotted, and the concentration of elements in the oxides are correct relative to one another, but not overall. The nanodispersoids are rich in Y, Al, and O while Fe and Cr are confined in the matrix. Titanium also surrounds the nanodispersoids suggesting initially the dispersoids have a core-shell structure. Because Al has a higher affinity for oxygen than Ti, Ti tends to become depleted from the oxides. A solute-enriched shell can occur if the rate of solute depletion from the oxide exceeds solute diffusion away from the interface during the consolidating heat treatment of the alloy [261].

The ratio of Y to Al in several oxides measured by EDS is shown in Figure 6.2. Since Al is present in the matrix (~ 11 at. %), Al values were corrected by taking into consideration the ratio of the oxide Feret diameter to the foil thickness. A linear fit of the data yields an estimated Y:Al ratio of 1.25. Based on composition, the nanodispersoids are likely to be either YAP or YAH. Atomic resolution STEM was used to determine the initial crystallographic structure of the nanodispersoids. Figure 6.3 shows high-resolution STEM (HR-STEM) HAADF of a nanodispersoid. The indexed fast Fourier transform (FFT) reveals that the nanodispersoids appeared to be fully crystalline YAP particles. While we cannot completely exclude the presence of YAG, YAM, or YAH nanodispersoids, we did not detect these other types of oxides when examining the microstructure with EDS and HR-STEM.

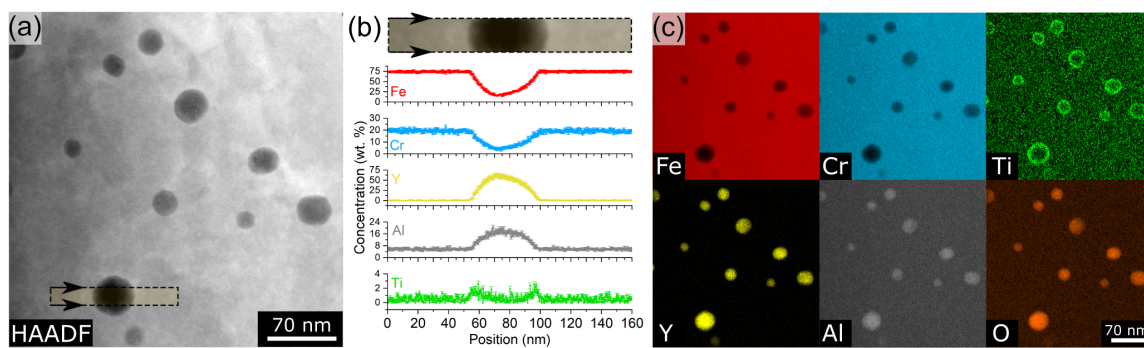


Figure 6.1: Chemical mapping of the non-irradiated nanodispersoids in PM2000 performed with high-throughput STEM-EDS. (a) HAADF image of the area mapped with EDS, (b) an EDS line scan measured across a nanodispersoid, and (c) the raw K_{α} X-ray count maps for Fe, Cr, Ti, Y, Al, and O.

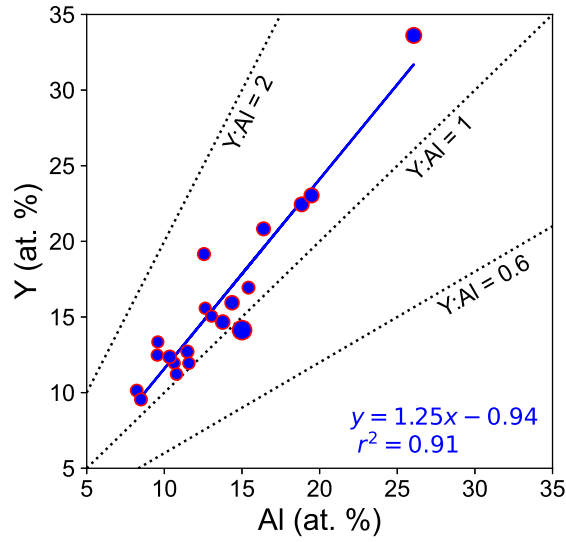


Figure 6.2: A comparison of the Y and Al concentrations in the non-irradiated nanodispersoids as measured with STEM-EDS. The Al concentrations are corrected to account for Al in the matrix, based on the TEM foil thickness. Lines for Y:Al = 0.6, 1, and 2 are plotted for reference, corresponding to the Y:Al in $Y_3Al_5O_{12}$, $YAlO_3$, and $Y_4Al_2O_9$, respectively. The diameter of each point corresponds to the Feret diameter of the measured oxide. A linear fit of the data is provided.

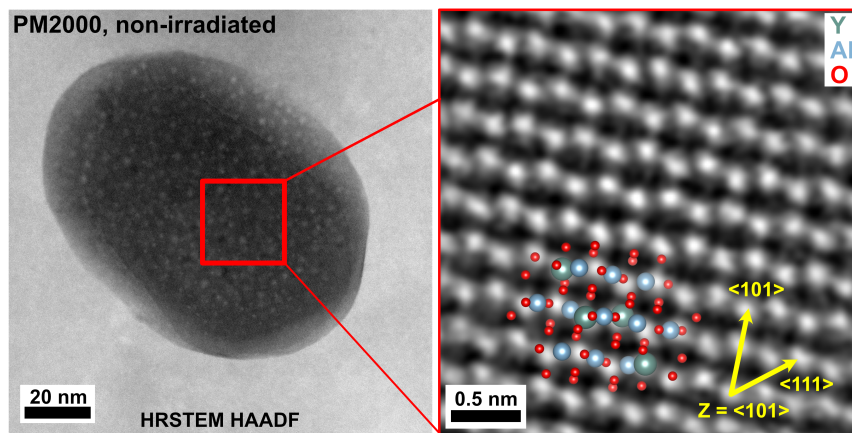


Figure 6.3: HR-STEM HAADF images of a non-irradiated nanodispersoid in PM2000 at low and high magnifications. The high magnification image was processed with an average background subtraction filter. Y, Al, and O atoms are overlaid. The oxide was identified as a fully crystalline YAP particle oriented along the $\langle 101 \rangle$ zone axis.

Chemistry and structure of the YAP nanodispersoids after 5.5 dpa neutron irradiation

After 5.5 dpa neutron irradiation at 335 °C, TEM lamella were fabricated from the irradiated specimens using focused ion beam milling. The size and density of the nanodispersoids was first examined with STEM. The average Feret diameter of the oxides was 28.9 ± 1.2 nm and the number density was $8.22 \pm 1.33 \times 10^{20} \text{ m}^{-3}$. Relative to the unirradiated nanodispersoids, there was no significant change in number density, but the irradiated dispersoids were larger in diameter.

Further characterization of the nanodispersoids was conducted with HR-STEM to determine if structural modifications occurred during irradiation. All the nanodispersoids that were observed appeared to be completely amorphous. An example of the mottled contrast observed while imaging the oxides with HR-STEM HAADF can be seen in Figure 6.4. The amorphization of the oxides may explain the size increase of the nanodispersoids.

EDS mapping of the nanodispersoids was also performed to identify any chemical changes around or within the particles. An example is given in Figure 6.5. The Ti shell that was present around the non-irradiated nanodispersoids appeared faintly after 5.5 dpa neutron irradiation. The ratio of yttrium to aluminum measured in the dispersoids was more scattered than before irradiation, and the average Y:Al increased to 1.47 ± 0.24 from 1.18 ± 0.13 . Thus, aluminum concentration in the dispersoids appears to decline with irradiation.

Chemistry and structure of the YAP nanodispersoids after 55.9 dpa neutron irradiation

The highest dose achieved for the PM2000 samples after HFIR irradiation was 55.9 dpa at 287 °C. A dramatic evolution of the chemistry and structure of the nanodispersoids was revealed during characterization. In STEM bright field (BF) and

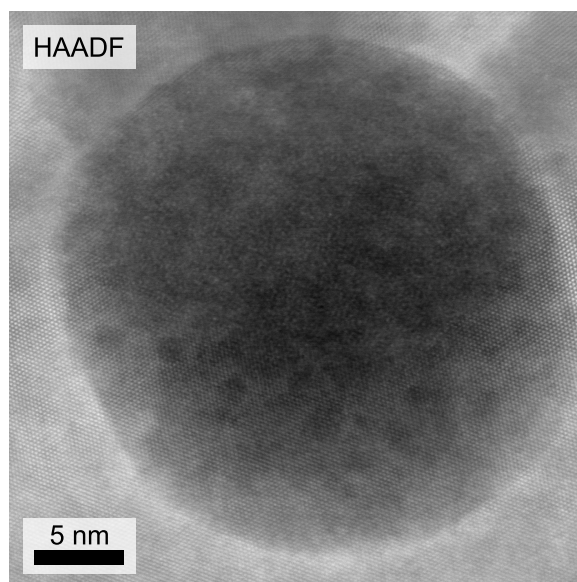


Figure 6.4: An HR-STEM HAADF image of a nanodispersoid in PM2000 irradiated to 5.5 dpa at 335 °C. The mottled contrast observed suggests the nanodispersoid lacks long range atomic structure and is amorphous.

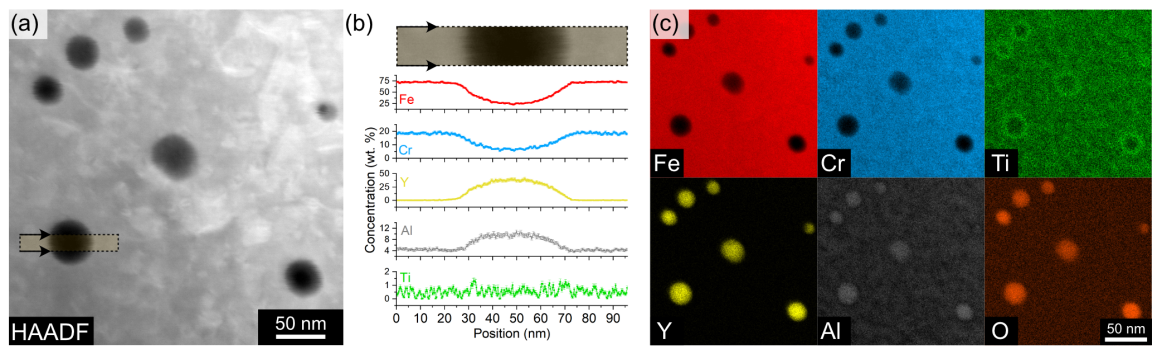


Figure 6.5: Chemical mapping of the nanodispersoids in PM2000 after neutron irradiated at 335 °C to 5.5 dpa. (a) HAADF image of the area mapped with EDS, (b) an EDS line scan measured across a nanodispersoid, and (c) the raw K_{α} X-ray count maps for Fe, Cr, Ti, Y, Al, and O.

HAADF imaging (Figure 6.6), there were circular regions within the nanodispersoids that showed noticeable brightness variations.

The contrast in HAADF suggests the presence of chemical inhomogeneities within the nanodispersoids. STEM-EDS mapping was performed to identify the chemistry of the bright subregions within the nano-dispersoids. The concentrations of Fe, Cr, Y, Al, and Ti concentrations measured from a line profile are provided in Figure 6.7b. Based on such EDS line profiles, the light subregions in HAADF within the nanodispersoids appear to be rich in Fe and Cr, while Y and Al are depleted. It is also notable that the enrichment of Ti originally observed at the nanodispersoid interfaces is no longer present.

Additional EDS line profiles across the nanodispersoids were measured over the dark subregions in HAADF. In these areas, there was very low X-ray signal, which confirms that the dark subregions are cavities. About 85% of the nanodispersoids appeared to develop a cavity. In all such cases, it was a single large cavity that appeared to preferentially occupy volume within the nanodispersoid, rather than the matrix. The average Feret diameter and number density of the cavities were 24.0 ± 1.0 nm and $2.44 \pm 0.27 \times 10^{20} \text{ m}^{-3}$, respectively.

The size distributions for nanodispersoids in the non-irradiated, 5.5 dpa, and 55.9 dpa neutron irradiated PM2000 are compared in Fig. 6.8. The size distribution of the cavities observed in the 55.9 dpa condition is also included. After high dose irradiation, the average Feret diameter and number density of the nanodispersoids were 31.2 ± 1.25 nm and $2.87 \pm 0.30 \times 10^{-20} \text{ m}^{-3}$, respectively. Thus, compared to the low dose neutron irradiation, the average size of the nanodispersoids increased while their number density decreased. Based on Figure 6.8, the number of oxides with Feret diameters ≤ 20 nm decreased as the size distribution shifted to larger sizes at the high dose. This may indicate the nanodispersoids experienced swelling due to cavitation, or simply that the nanodispersoids coarsened with neutron irradiation dose.

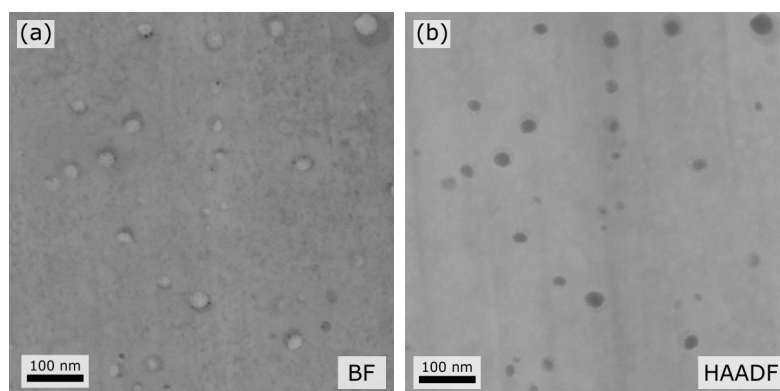


Figure 6.6: Low magnification (a) STEM-BF and (b) STEM-HAADF imaging of the nanodispersoids in PM2000 after neutron irradiation at 287 °C, 55.9 dpa.

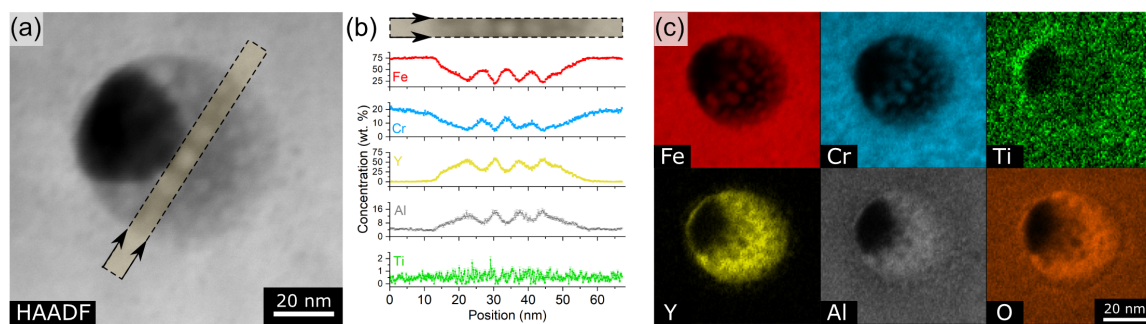


Figure 6.7: Chemical mapping of the nanodispersoids in PM2000 after neutron irradiated at 287°C to 55.9 dpa. (a) HAADF image of the area mapped with EDS, (b) an EDS line scan measured across a nanodispersoid, and (c) the raw K_{α} X-ray count maps for Fe, Cr, Ti, Y, Al, and O.

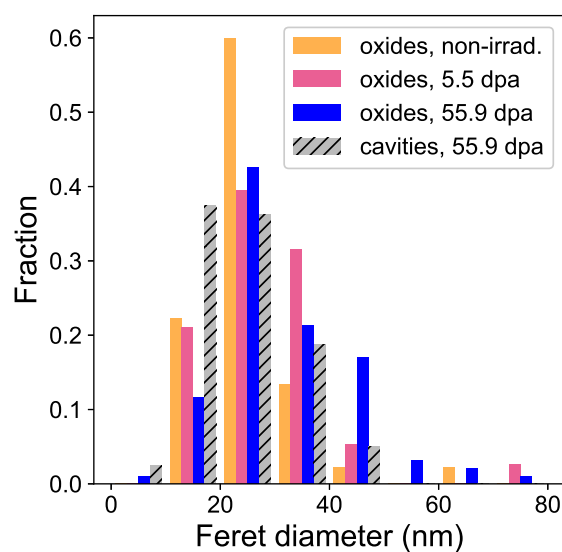


Figure 6.8: Nanodispersoid size distributions for the non-irradiated, low-dose, and high-dose neutron-irradiated PM2000. Sizes are measured by Feret diameter. The size distribution of cavities observed at 55.9 dpa is also plotted.

The brightness variations within the nanodispersoids observed in BF (Figure 6.6a) indicate the Fe-Cr-rich regions also have a unique crystallography. For further information, structures of the nanodispersoids were examined with HR-STEM HAADF. Atomic resolution images were scanned with an analysis window to collect local FFTs [262]. Key crystallographic components in the image were then identified with non-negative matrix factorization (NMF), as shown in Figure 6.9. The results show that the Y-Al-O portions of the nanodispersoids are completely amorphous, since no diffraction spots in the component FFT were detected. On the other hand, the Fe-Cr-rich subregions in the nanodispersoids and the Fe-Cr-Al matrix were identified by separate component FFTs. While they both have bcc structures with similar lattice parameters ($a_0 \approx 2.87 \text{ \AA}$), the orientation of each appears to be distinct. For example, in Figure 6.9, the Fe-Cr-Al matrix is aligned on the $\langle 110 \rangle$ zone axis while, by contrast, the Fe-Cr-rich island is not aligned along a low-index zone. A rotation of $\sim 28^\circ$ is visible between $\{110\}$ planes of the Fe-Cr-rich island and the Fe-Cr-Al matrix. Overall, no consistent orientation relationship between the Fe-Cr-rich crystalline islands and the Fe-Cr-Al matrix was evident. The average Feret diameter of the islands was $5.9 \pm 0.2 \text{ nm}$, and the estimated volume fraction they occupied within each nanodispersoid, assuming the islands are spherical, was $\sim 2 - 7 \%$.

6.1.2 Instability of pyrochlore nanodispersoids in MA957

Given the observations of oxide damage in PM2000, the nanodispersoids in MA957 were also characterized by STEM-EDS and HRSTEM before and after irradiation. Initially, the microstructure of MA957 contains $\text{Y}_2\text{Ti}_2\text{O}_7$ pyrochlores that are generally between ~ 15 and 35 nm in diameter, and Y-Ti-O nanoclusters, which are smaller [104]. The pyrochlore oxides were predominately distributed near and along grain boundaries, while the high density of nanoclusters were typically dispersed in the grain interiors. STEM BF and ADF images of the nanodispersoids at low magnification are given in Figure 6.10a–b. The Y-Ti-O nanoclusters were hard to identify by TEM,

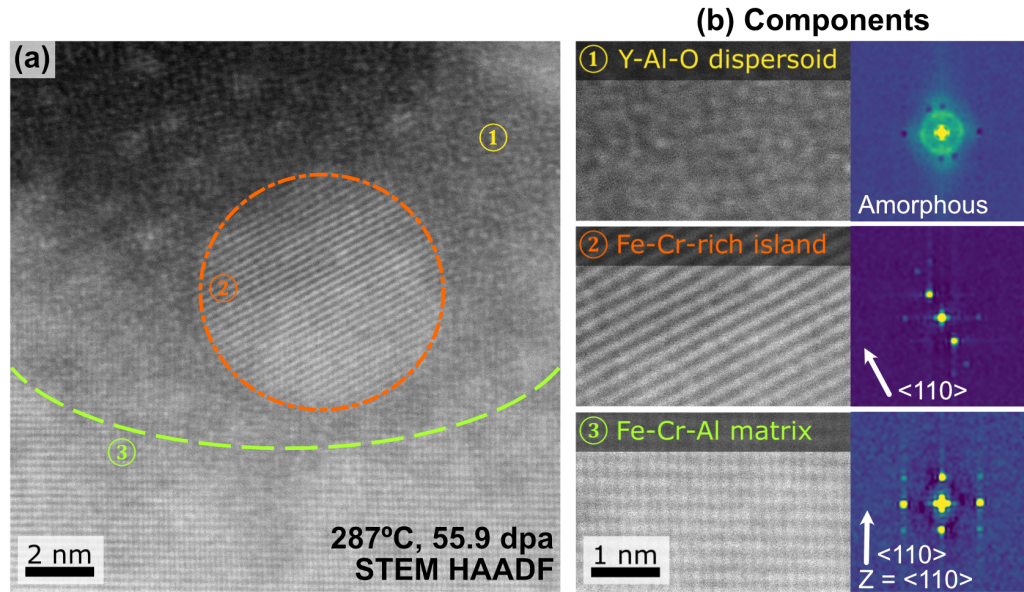


Figure 6.9: (a) An HRSTEM HAADF image showing a portion of a neutron irradiated nanodispersoid. Local FFTs were collected from the image using a sliding window (256 x 256 pixels). NMF was then used to identify principal FFT components within the image. (b) The image contains three components: (1) an amorphous Y-Al-O dispersoid, (2) a Fe-Cr-rich island with $\{110\}$ planes visible ($d = 2.03 \text{ \AA}$), and (3) the Fe-Cr-Al matrix oriented on the $\langle 110 \rangle$ zone axis.

but were readily apparent by APT (see Section 5.1.2). Due to the difficulties of performing advanced characterization on the Y-Ti-O nanoclusters, TEM observations were focused on the pyrochlore oxides. The structure of the nanodispersoids was confirmed by HRSTEM (see Figure 6.10c–d). STEM-EDS of the oxides prior to irradiation, see Figure 6.2e–f, confirms that the particles are composed uniformly of Y and Ti. The Y/Ti atomic ratios measured by EDS were close to 1, suggesting the oxides $>\sim 7$ nm in diameter are likely to be stoichiometric.

After 5.1 – 8.6 dpa neutron irradiation at 335 – 500 °C, HRSTEM imaging (Figure 6.11) revealed that the particles had amorphized. For the 335 and 450 °C conditions, all observed particles were fully amorphous. In addition to mottled contrast, no spots belonging to the oxides were detected in the diffractograms. However, for the 500 °C condition, a few of the larger oxides appeared to be partially crystalline. Figure 6.12 gives one such example. The abundance of each component diffractogram determined by NMF is mapped, showing the interface of the oxide is amorphous, while the center of the oxide retains its pyrochlore structure. This suggests that the critical amorphization temperature of the $\text{Y}_2\text{Ti}_2\text{O}_7$ pyrochlores subjected to neutron irradiation may be slightly higher than 500 °C.

STEM-EDS line profiles of the oxides irradiated 5.1 – 8.6 dpa neutron irradiation at 335 – 500 °C are given in Figure 6.13. No distinct pockets of Fe or Cr were detected in the oxides. At 500 °C and to some extent at 450 °C, titanium accumulates at the interface of the oxides. In addition, Ni also segregates to similar locations as Ti along the oxide interface (see Section 5.1.2). The corners of the oxides, because of their high surface area per volume, were preferential sites for Ni-Ti-enriched clustering [263].

At even higher doses, 51.5 dpa, at 287 °C the nano-oxides in MA957 were further degraded. Like the oxides in PM2000, many of the nano-oxides had developed a cavity and Fe-rich crystalline islands. STEM BF, HAADF, and EDS maps collected from two different oxides are given in Figure 6.14. The line scans taken across the oxides confirm that the bright regions in HAADF correspond to Fe-rich features. Unlike in PM2000, a significant concentration of Cr was not detected in the island regions. This

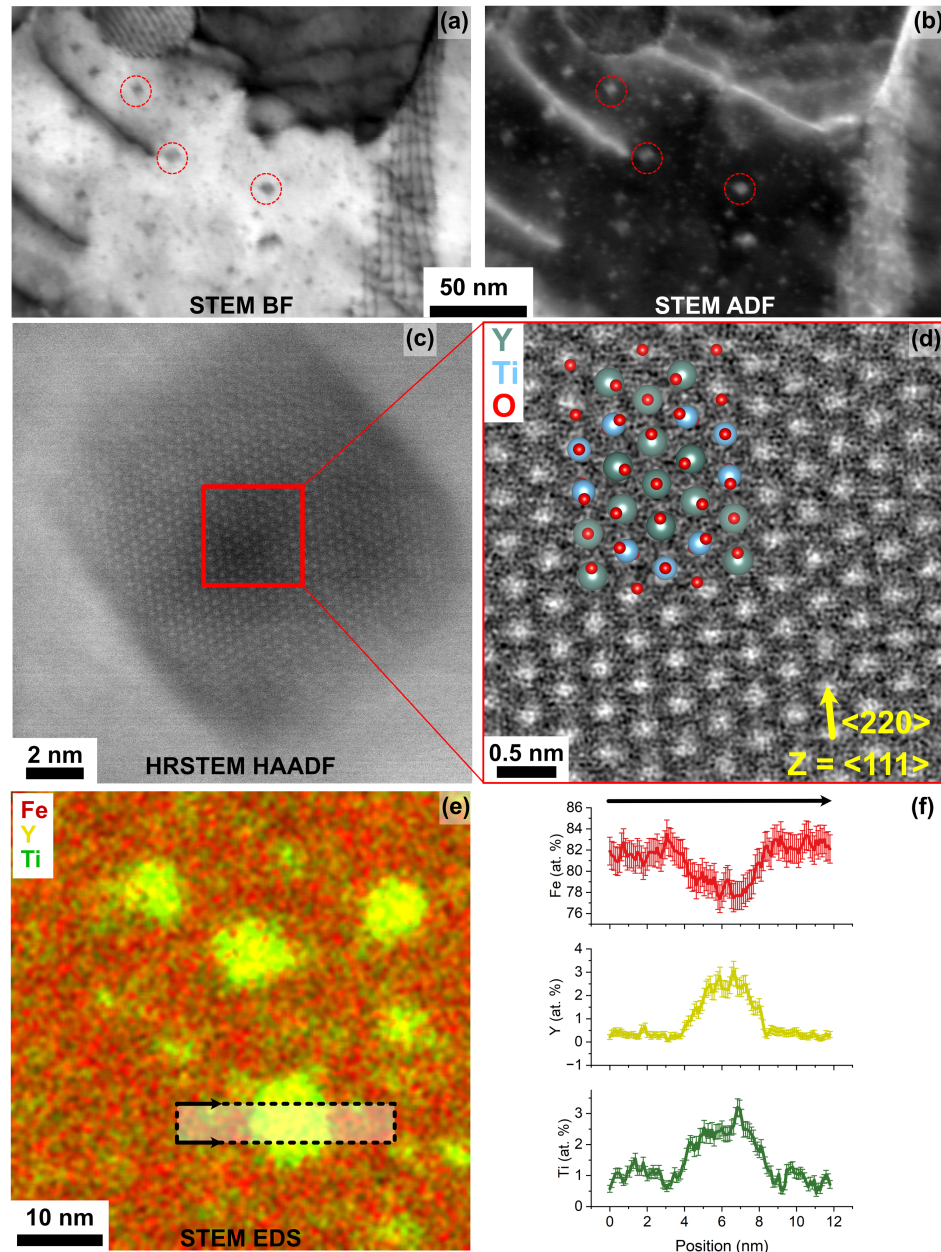


Figure 6.10: The structure and chemistry of nanodispersoids in MA957 prior to irradiation. (a) STEM BF and (b) STEM ADF images of the microstructure, showing the spatial distribution of the oxides (a few examples are circled). (c) HRSTEM HAADF of an oxide particle showing its crystalline structure. (d) High magnification of a select area of the oxide where the interplanar spacing and symmetry is consistent with the $\langle 111 \rangle$ zone axis of a pyrochlore. Image processing was done with an average background subtraction filter. (e) A STEM EDS map quantified by weight percent showing the initial distribution of Fe, Y, and Ti and (f) quantified line scan data across the region labeled in (e).

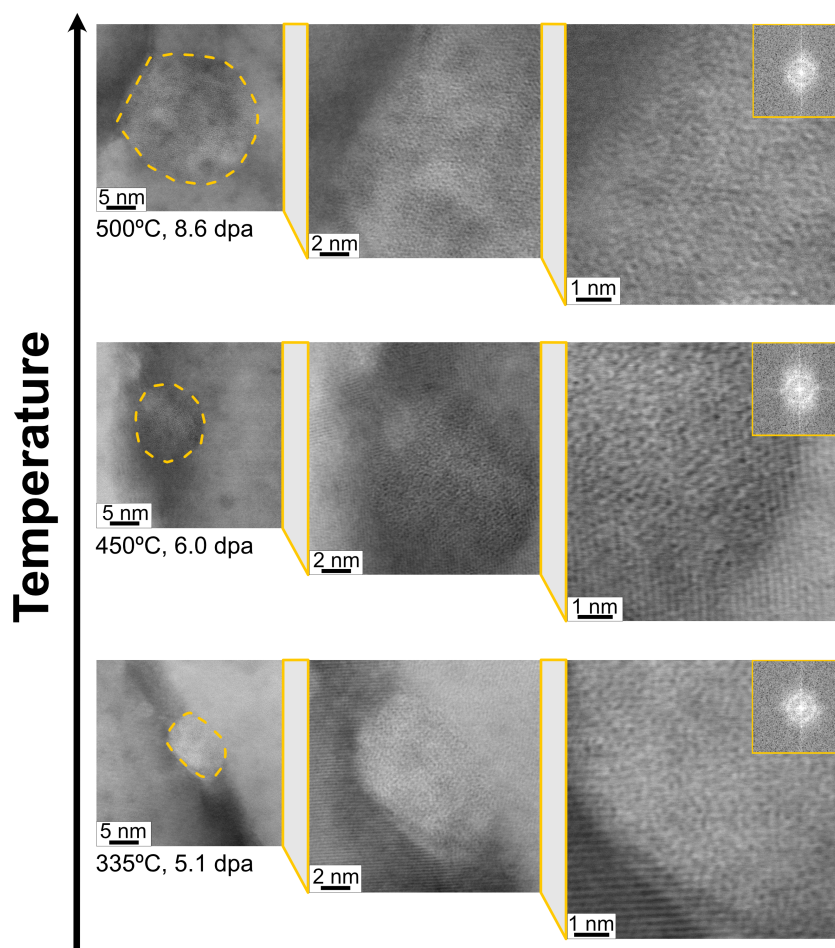


Figure 6.11: Structure of the oxides in MA957 after low dose (5.1 – 8.6 dpa) neutron irradiation as imaged with HRSTEM ABF. Oxides are encircled with dotted lines in the low magnification images. Between 335 and 450 °C, FFTs indicate the oxides were amorphous. At 500 °C, most of the smaller oxides were also amorphous.

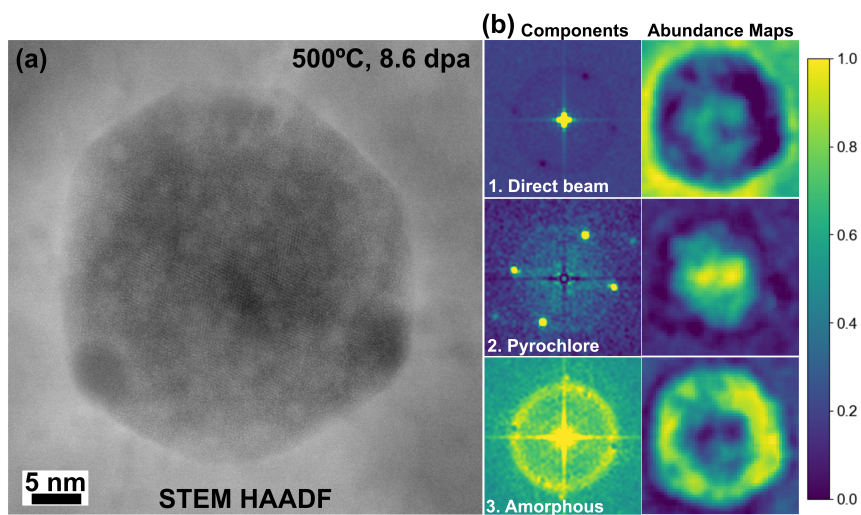


Figure 6.12: A partially amorphous oxide particle imaged in MA957 after irradiation in HFIR to 8.6 dpa at 500 °C. (a) An HRSTEM HAADF image of the oxide particle (b) Results from a NMF of FFTs collected from the image. Three components are identified: (1) the direct beam, (2) crystalline regions in the pyrochlore, and (3) an amorphous region at the oxide interface. The component diffractograms are shown and the abundance of each component in the image is mapped.

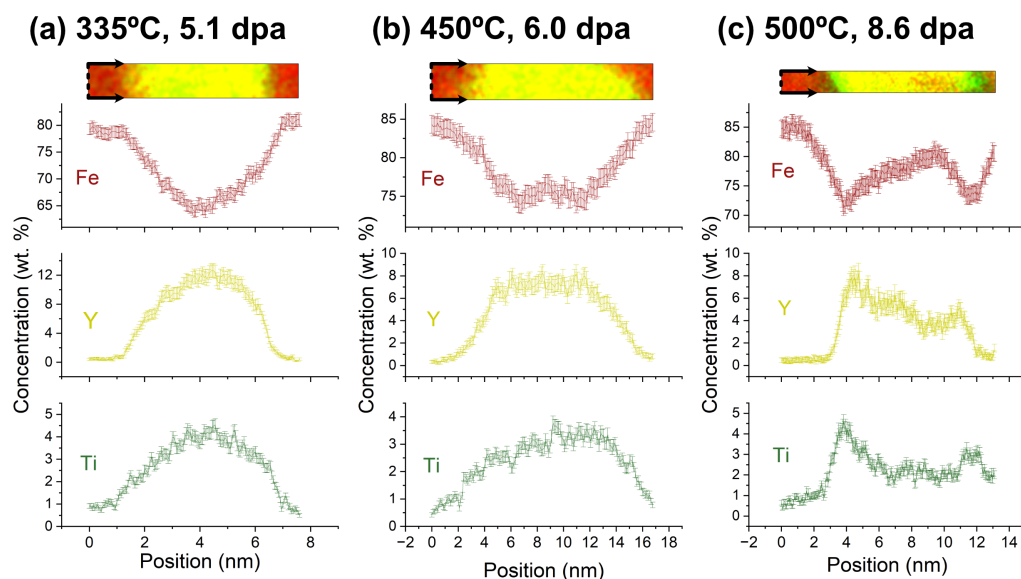


Figure 6.13: EDS line scans measured across the oxides in MA957 quantifying the concentration of Fe, Y, and Ti after low dose neutron irradiation. Results for (a) 335 °C, 5.1 dpa, (b) 450 °C, 6.0 dpa, and (c) 500 °C, 8.6 dpa. At 500 °C, segregation of Ti to the oxide interface is detected.

may be because MA957 has a lower bulk Cr concentration than PM2000 or because a much higher fraction of Cr was partitioned into solute clusters in the high-dose neutron irradiated MA957 compared to PM2000 (~ 24.0 at.% vs 4.4 at.%).

From HRSTEM, the d-spacings measured from these crystalline islands match well with those expected for bcc-Fe. An example of the typical oxide structures observed is given in Figure 6.15. FFTs collected by a sliding window from the HRSTEM HAADF image were analyzed with NMF. In Figure 6.15c, the resulting FFT components show the matrix is off-zone, but the (211) planes of the crystalline island are visible. The light region in the STEM ABF image corresponds to a cavity. It should also be noted that surrounding the oxide particle, there are several amorphous regions. The presence of these regions is reminiscent of the halos observed around ballistically damaged oxides in alloy DY after irradiation in Phénix [139, 138]. These satellite particles may be evidence of ballistic dissolution and re-precipitation.

6.2 Discussion

6.2.1 Ballistic introduction of Fe into the nanodispersoids

Traditional models for nanoparticle stability under irradiation such as those by Nelson, Hudson, and Mazey [227], Frost and Russell [264], or Heinig et al. [43], focus on the combined effects of radiation enhanced diffusion (RED) and ballistic mixing to predict changes in particle size. Thus, processes like Ostwald ripening, radiation enhanced coarsening, inverse Ostwald ripening, or ballistic dissolution can be modelled. However, a weakness of the aforementioned models is that ballistic mixing of the atoms is considered to be unidirectional, meaning solute atoms can only be transported from the particle into the matrix. In the high-dose neutron irradiated PM2000 and MA957, the observed Fe-rich islands in the Y-Al-O and Y-Ti-O nanodispersoids, respectively, suggest the opposite process might also occur: atoms can be ballistically transported into the particle from the matrix.

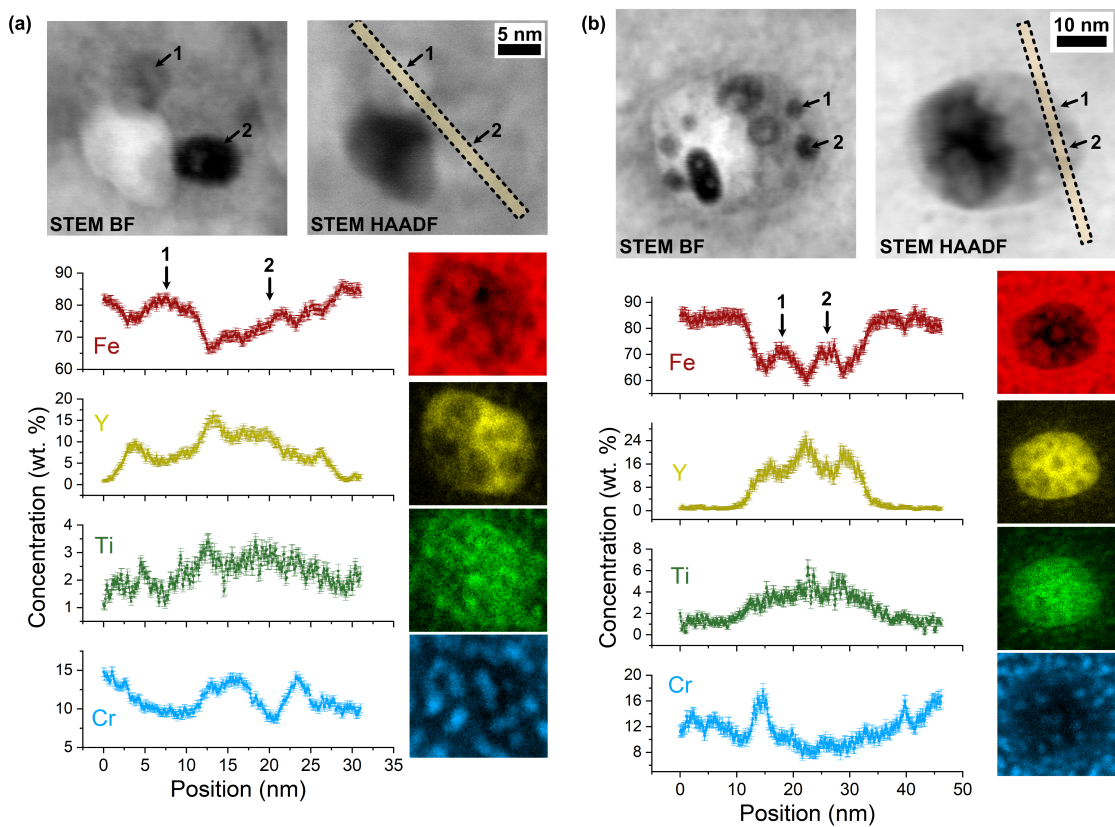


Figure 6.14: STEM BF and HAADF imaging as well as EDS maps of two different oxides in MA957 after neutron irradiation in HFIR at 287 °C to 51.5 dpa. EDS maps in (a) and (b) are quantified by weight percent. Concentration profiles of Fe, Y, Ti, and Cr were measured across the regions highlighted in the HAADF images.

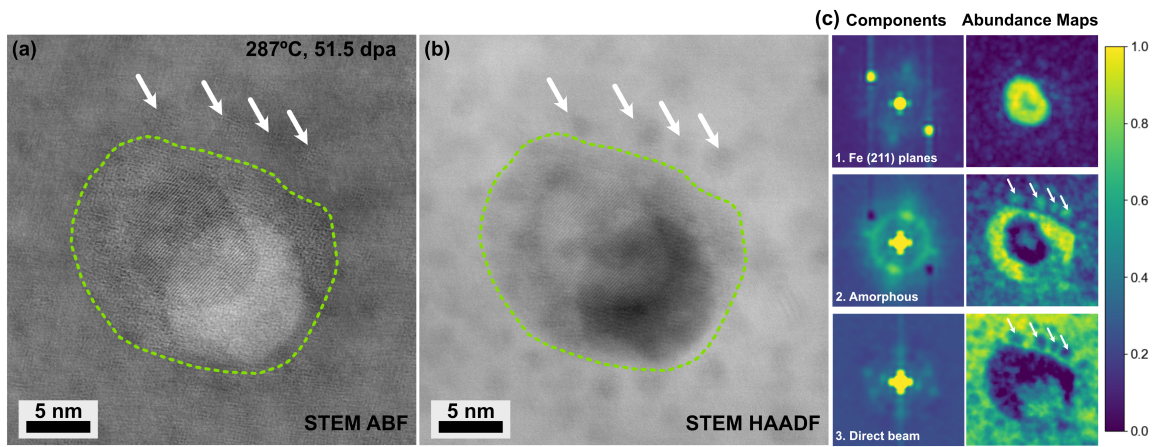


Figure 6.15: HRSTEM imaging showing the structure of an oxide in MA957 after neutron irradiation at 287 °C to 51.5 dpa. (a) HRSTEM ABF, (b) HRSTEM HAADF, and (c) the three main components identified by NMF of FFTs collected from the HAADF image. The intensity of each component FFT across the image is provided in the abundance maps. White arrows indicate the amorphous satellite particles that were detected around the main particle.

For a simple A-B alloy, Shu et al. performed kinetic Monte Carlo (KMC) simulations to find the irradiation conditions where a stable sub-structure can form [265]. They found that A-rich “cherry-pits” are more likely to form in B-rich precipitates at low ballistic jump frequencies, i.e. low irradiation damage rates, if the solubility or diffusivity of A in B is lower compared to B in A. Compared to metal-metal systems, it is more difficult to predict threshold damage rates for sub-structure formation in oxide-metal systems. Whereas two metals can form a random solid solution, the energy involved with introducing a metal atom into a ceramic structure and the solute atom’s subsequent migration depends significantly on site occupancy within the ceramic structure. Here we consider the energetics of Fe ballistically injected into YAP with DFT modelling.

If a Fe atom is ballistically injected into a YAP nanodispersoid, it is energetically favorable for that Fe atom to occupy a vacant Al site. DFT modelling results given in Table 6.1 indicate that the reaction where a bulk Fe atom fills an Al vacancy in the YAP structure ($\text{Fe}_{x+1}^{\text{Fe}} + \text{V}_{\text{Al}}^{\text{YAP}} \longrightarrow \text{Fe} + \text{Fe}_{\text{Al}}^{\text{YAP}}$) lowers the system energy by 6.86 eV. If the Fe atom previously occupied an interstitial site in the matrix ($\text{Fe}_{\text{i}}^{\text{Fe}} + \text{V}_{\text{Al}}^{\text{YAP}} \longrightarrow \text{Fe} + \text{Fe}_{\text{Al}}^{\text{YAP}}$), it is even more energetically favorable, since 10.92 eV is released when the Al vacancy is filled.

It is common for some vacancies to be present in nanodispersoids after alloy fabrication [266]. Additional vacancies will be formed in the nanodispersoids by displacement events during irradiation. The concentration of point defects in a ceramic typically saturates at $\sim 1 - 5$ at. % in the point defect swelling temperature regime, which is the temperature range where there is long-range migration of interstitials but not vacancies (between ~ 0.05 and 0.3 times the melting temperature) [30]. Therefore, considering the estimated volume fraction of the Fe-Cr-rich islands in the neutron irradiated PM2000 nanodispersoids ($\sim 2 - 7$ %) and that only a fraction of the point defects produced in YAP will be Al vacancies, it seems likely that the concentration of injected Fe and Cr exceeds the Al vacancy concentration at high irradiation doses. Due to forced ballistic mixing during irradiation, Fe atoms

may also enter the YAP structure by substitutional or interstitial reactions. Unlike vacancy filling, these other interactions, discussed in the following section, may incur a substantial energy penalty.

6.2.2 Structural transformation of the nanodispersoids

During neutron irradiation, nanodispersoids in PM2000, which were originally YAlO_3 perovskites, and nanodispersoids in MA957, which were originally $\text{Y}_2\text{Ti}_2\text{O}_7$ pyrochlores, were amorphized. For single phase materials, traditional models for irradiation-induced amorphization include the direct impact and cascade overlap models [49, 47]. In the direct impact model, defects (vacancies, interstitials, anti-site defects, etc.) formed during the displacement cascade event destabilize the crystal structure and cause amorphization. The cascade overlap model is similar to the direct impact model, however, the critical defect concentration required to cause amorphization accumulates over multiple cascade events rather than a single one.

Alternatively, for composite materials, ballistic mixing can produce chemical shifts at interfaces that can stabilize the amorphous state [267]. In our study, ballistically injected Fe and Cr may further raise the free energy of the nanodispersoids, promoting the particles to amorphize. A similar effect was proposed by Motta and Lemaignan to explain the amorphization of intermetallic $\text{Zr}(\text{Fe,Cr})_2$ precipitates in neutron irradiated Zircaloy [268]. As presented in Table 6.1, DFT calculations indicate that reactions where Fe enters the YAP structure as an interstitial or substitutional atom are unfavorable since they are highly endothermic. For the reaction where an interstitial Fe atom in the Fe bulk enters the YAP structure as an interstitial ($\text{Fe}_i^{\text{Fe}} + \text{YAP} \longrightarrow \text{Fe} + \text{YAP} + \text{Fe}_i^{\text{YAP}}$), the energy of the system is raised by 3.10 eV. However, if the Fe atom is originally in a lattice site and then enters the YAP structure as an interstitial ($\text{Fe}_{x+1}^{\text{Fe}} + \text{YAP} \longrightarrow \text{Fe} + \text{YAP} + \text{Fe}_i^{\text{YAP}}$), the reaction increases the energy of the system by 7.16 eV. Another potential reaction pathway is that a Fe atom occupying a lattice site in the bulk could substitute with an Al

Table 6.1: Reaction energies calculated by DFT

Reaction	Energy (eV)	Description
$\text{Fe}_{x+1}^{\text{Fe}} + \text{V}_{\text{Al}}^{\text{YAP}} \longrightarrow \text{Fe} + \text{Fe}_{\text{Al}}^{\text{YAP}}$	-6.86	lattice Fe filling an existing Al vacancy in YAP
$\text{Fe}_i^{\text{Fe}} + \text{V}_{\text{Al}}^{\text{YAP}} \longrightarrow \text{Fe} + \text{Fe}_{\text{Al}}^{\text{YAP}}$	-10.92	interstitial Fe filling an existing Al vacancy in YAP
$\text{Fe}_i^{\text{Fe}} + \text{YAP} \longrightarrow \text{Fe} + \text{YAP} + \text{Fe}_i^{\text{YAP}}$	3.10	interstitial Fe forming a Fe interstitial in YAP
$\text{Fe}_{x+1}^{\text{Fe}} + \text{YAP} \longrightarrow \text{Fe} + \text{YAP} + \text{Fe}_i^{\text{YAP}}$	7.16	lattice Fe forming a Fe interstitial in YAP
$\text{Fe}^{\text{Fe}} + \text{YAP} \longrightarrow \text{Al}_{\text{Fe}} + \text{YFe}_x\text{Al}_{1-x}\text{O}_3$	3.99	lattice Fe in substituting with Al in YAP
$\text{Fe}^{\text{Fe}} + \text{YAP} \longrightarrow \text{Y}_{\text{Fe}} + \text{Y}_{1-x}\text{Fe}_x\text{AlO}_3$	9.02	lattice Fe in substituting with Y in YAP

atom in the YAP ($\text{Fe}^{\text{Fe}} + \text{YAP} \longrightarrow \text{Al}_{\text{Fe}} + \text{YFe}_x\text{Al}_{1-x}\text{O}_3$), which would raise the energy of the system by 3.99 eV. Finally, Fe could also substitute with Y in YAP ($\text{Fe}^{\text{Fe}} + \text{YAP} \longrightarrow \text{Y}_{\text{Fe}} + \text{Y}_{1-x}\text{Fe}_x\text{AlO}_3$), however the energy penalty for this is 9.02 eV, which is significantly higher than for the Fe-Al substitution reaction. These highly unfavorable reactions may occur if the amount of injected Fe exceeds the Al vacancy concentration, or if injected Fe is unable to reach a vacant Al site.

Little literature exists on activation energies and critical temperatures for the crystalline-to-amorphous transition of YAP. In another study of PM2000 neutron irradiated at 500 °C for ~ 21 dpa, the oxides were similarly completely amorphous [141]. For perovskites, amorphization susceptibility appears to vary significantly with chemistry [51]. However, the exact factors that dictate phase stability of perovskites are unknown. Bond covalency may play some role, since covalent oxides tend to have greater amorphization susceptibility than ionic oxides [269]. In addition, amorphization resistance may roughly correlate to the Goldschmidt tolerance factor of a perovskite [270], which measures structural distortion. This is because the energy to form an anti-site defect generally increases with tolerance factor [54]. One might expect YAlO_3 to have amorphization resistance comparable to SrTiO_3 because both have similar bond polarities and Goldschmidt tolerance factors (~ 0.86 for YAlO_3 and ~ 1.00 for SrTiO_3). However, Meldrum et al. reported that for 800 keV Kr^+ irradiations, the critical amorphization temperature of SrTiO_3 was 152 °C [51]. In addition, critical amorphization temperature during neutron irradiations should be less than during ion irradiations because dose rates are normally lower [271, 272]. The fact that the nanodispersoids in neutron irradiated PM2000 were able to be amorphized at 287 and 500 °C (Ref. [141]) suggests that ballistically injected Fe and Cr may contribute to the structural instability of YAP. This follows the behavior of other oxides, where metal impurities also been shown to increase amorphization susceptibility [273, 274].

Unlike for YAP, there are studies specifically aimed at understanding the amorphization of $\text{Y}_2\text{Ti}_2\text{O}_7$ pyrochlores. Both Lian et al. and Whittle et al. have

conducted 1 MeV Kr^+ irradiations on $\text{Y}_2\text{Ti}_2\text{O}_7$ at the IVEM facility at Argonne National Laboratory [275, 276]. Lian et al. determined a critical amorphization temperature of 507°C , while Whittle et al. reported a value of 392°C . Since the nanodispersoids in MA957 were amorphous after neutron irradiation at temperatures as high as 500°C , their susceptibility to amorphization was greater than anticipated based on ion irradiation experiments. For pyrochlore oxides ($\text{A}_2\text{B}_2\text{O}_7$), the radius ratio between the A and B cation, r_A/r_B , is known to affect structural stability, since the energy required to form an antisite defect increases with r_A/r_B [275]. Thus, as r_A/r_B approaches unity, the pyrochlore structure is expected to be more irradiation tolerant. Assuming ballistically injected Fe prefers to fill a B cation site, the ionic radius of Fe^{4+} is smaller than the radius of Ti^{4+} , and so its introduction would increase r_A/r_B [277]. The amorphous interface and crystalline core observed for some particles after 500°C irradiation further supports the hypothesis that the amorphization susceptibility of the nano-oxides is enhanced by ballistic mixing of Fe from the matrix.

Amorphization of the nano-dispersoids may exacerbate mixing of Fe and Cr into and within the particles as irradiation progresses. For example, Cooper and Nastasi have demonstrated that at low temperatures ($T < 400^\circ\text{C}$), ballistic mixing of a crystalline Fe_2O_3 marker layer was four times greater in amorphous alumina compared to crystalline alumina (sapphire) [278]. Similarly, for ion irradiations between 27 and 427°C , Scheuer et al. observed greater spreading of a Hf marker layer in an amorphous Fe-37 at.% Ti film compared to a crystalline film of the same composition [279]. Additional ballistic mixing in amorphous versus crystalline semiconductors may occur during the cascade relaxation process, as atoms displaced short distances forget their original locations and settle into sites of local minimum potential energy [280]. Apart from radiation mixing, thermal diffusion may also be greater in amorphous compared to crystalline solids, as entropies of diffusion are typically much higher as a result of the extended nature of defects in glassy systems [281].

The driving force leading Fe and Cr to precipitate in the amorphous oxides is an interesting area that requires further investigation. One possibility is that free

electrons created during neutron irradiation are responsible for reducing Fe and Cr impurity cations, which enables their agglomeration. To date, gamma, X-ray, electron, and ion irradiation have all been used as a means to produce metal colloids in doped glasses [282, 283, 284, 285, 286]. Since Fe^{3+} and Cr^{3+} both have higher standard potentials than Y^{3+} , Al^{3+} , and Ti^{4+} , these impurity ion species in YAlO_3 or $\text{Y}_2\text{Ti}_2\text{O}_7$ are expected to be preferentially reduced by free electrons [287]. To our knowledge, there are no experimental reports specifically of metal colloids forming in amorphous YAlO_3 or $\text{Y}_2\text{Ti}_2\text{O}_7$ under irradiation. Nonetheless, absorption spectra measured from neutron and gamma irradiated YAP crystals confirm that Fe impurities are reduced, likely by a combination of $\text{O}_2^- + h\nu \longrightarrow \text{O}^- + \text{e}^-$ and $\text{Fe}^{3+} + \text{e}^- \longrightarrow \text{Fe}^{2+}$ reactions [288]. When neutralized, impurity atoms may easily diffuse in the amorphous oxides and agglomerate.

The hypothesized mechanism for the structural and chemical transformation of the nanodispersoids is summarized schematically in Figure 6.16. Prior to irradiation, the oxides are fully crystalline and do not contain either Fe or Cr in significant concentrations. During neutron irradiation, the oxides first amorphize, a process which is assisted by the ballistic mixing of matrix atoms. Then cavity formation occurs due to the agglomeration of vacancies and free volume while Fe and Cr continue to be ballistically mixed into the oxide. Finally, the reduction of Fe and Cr in the oxide enhances their diffusivity, and the ballistically injected atoms may precipitate as crystalline islands within the body of the amorphous oxide.

Given the dramatic structural and chemical evolution of the nanodispersoids at $\sim 300^\circ\text{C}$, and the amorphization of the $\text{Y}_2\text{Ti}_2\text{O}_7$ pyrochlores up to 500°C , these particles do not appear to be stable after neutron irradiation. This conclusion is in contrast to several published neutron irradiation studies of ODS in literature (see Figure 2.6). However, many studies such as Refs. [133, 145, 149, 147, 152] have based their assessment of phase stability solely around changes in oxide size and number density. Thus, the structural and chemical evolution of the nanodispersoids is often neglected. Characterization techniques may also limit what phase stability determinations can

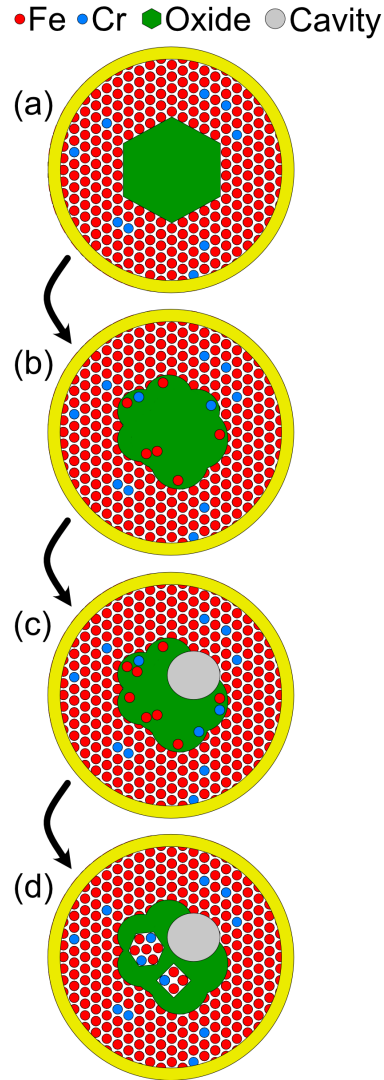


Figure 6.16: A diagram depicting the hypothesized mechanism for the structural and chemical transformation of the nanodispersoids. (a) Prior to irradiation, the oxides are fully crystalline, and there is little to no Fe or Cr inside the oxides. During neutron irradiation, (b) the ballistic mixing of Fe and Cr into the oxide contribute to the amorphization of the oxides, (c) vacancy and free volume agglomeration drive cavity formation, and (d) the ballistically injected atoms may be reduced and precipitate as crystalline islands in the amorphous oxides.

be made. For example, studies using only APT, such as Refs. [136, 135, 134, 148, 154], do not give insight on oxide crystallographic structure post-irradiation. When sink strength, structure, and chemistry are comprehensively examined, however, such as in Ref. [139, 138, 150] and this study, the results suggest that the oxides are in fact not completely stable.

6.2.3 Internal cavity formation in oxide particles

For the PM2000 neutron irradiated at 287 °C to 55.9 dpa, about 85% of the nanodispersoids developed a cavity that appeared to form primarily in the oxide. On the other hand, at 335 °C 5.5 dpa, there were very few cavities observed. Likewise, in the MA957, a sparse number of cavities were observed at low dose, between 5.1 – 8.6 dpa, and 335 and 500 °C, while at the highest dose examined, 51.5 dpa, many oxides had internal cavities. The doses at which cavitation was observed in PM2000 and MA957 suggests that cavity formation in ODS alloys during neutron irradiation requires an incubation period.

The cavity microstructure that develops in ODS alloys under irradiation depends significantly on the character of the matrix-oxide interface. For semicoherent nanodispersoids, misfit dislocations act as He trapping sites. As a result, bubbles tend to form periodically around the oxides. The aforementioned cavity microstructure is in contrast to the one observed in the neutron-irradiated PM2000 and MA957, where many dispersoids had a single large cavity. Based on their size, one would expect the nanodispersoids in PM2000 to be incoherent. Unlike semicoherent interfaces, the behavior of He at incoherent interfaces is less well-known. In many respects, incoherent interfaces are akin to high angle grain boundaries [289]. As a result, one may expect the large excess volume at the interface to support fast diffusion of He and vacancies. At grain boundaries in helium implanted copper, Thorsen et al. observed that as boundary energy increased, bubble size tended to increase while

density decreased [290]. Hence, at interfaces of sufficiently high energy, rapid kinetics may promote growth of existing cavities over nucleation.

Across the many nanodispersoids examined in neutron-irradiated PM2000, almost all the cavity volume appeared to overlap with the nanodispersoids. While TEM analysis only provides a two-dimensional prospective, this overarching trend suggests that the cavities grow inside the nanodispersoids rather than attached to the surface. Such cavity growth into the oxide may be a swelling concern. This is because surface energies for oxides are lower than for metals, and so the critical radius for a helium bubble to convert to a void subject to bias driven growth will be lower in the nanodispersoid compared to the matrix [291, 292]. Thus, cavity growth into the oxide may reduce the incubation period for swelling.

In ferritic ODS alloys, helium is generated primarily by the transmutation of Fe in the matrix. The nanodispersoid interfaces trap the produced helium, which leads to accumulation and bubble formation. Since metal-oxide interfacial energies are typically much lower than metal surface energies, bubbles will preferentially nucleate attached to the nanodispersoids. As an estimate, the interfacial energies of coherent $\text{Y}_2\text{Ti}_2\text{O}_7$ and Y_2O_3 nanodispersoids in ferritic ODS alloys are $\sim 0.26 \text{ J/m}^2$ and 0.35 J/m^2 [293], respectively, while the surface energy of alpha iron is $\sim 2.47 \text{ J/m}^2$ [294]. Compared to alpha iron, surface energies of most oxides are also lower. It will be demonstrated that under these conditions, a cavity can grow into both the metal and oxide phases if the metal-oxide interfacial energy is above a threshold value. The metal, oxide, and cavity then exist in three-phase equilibrium.

Using an analogy to wetting behavior [295, 296], the critical interfacial energy for three-phase equilibrium can be determined with Neumann's triangle construction, shown schematically in Figure 6.17. Here $\gamma_{A/C}$ is the interfacial energy between the metal and cavity, $\gamma_{B/C}$ is the interfacial energy between the oxide and cavity, and $\gamma_{A/B}$ is the interfacial energy between the metal and oxide. Based on the triangle inequality theorem, the condition for internal cavitation becomes apparent as three-phase equilibrium requires $\gamma_{A/B} \geq \gamma_{A/C} - \gamma_{B/C}$. For the neutron-irradiated PM2000,

we assume for simplicity that the cavity is a void without any helium, and so the surface energies for Fe and YAP, σ_{Fe} and σ_{YAP} , can be used in lieu of $\gamma_{A/C}$ and $\gamma_{B/C}$, respectively. The minimum interfacial energy for internal cavitation is therefore calculated to be 0.4 J/m² assuming $\sigma_{Fe} = 2.47$ J/m² [294] and $\sigma_{YAP} = 2.07$ J/m² [297]. This falls in the range of values expected for semi-coherent interfaces.

Based on this result, it is not surprising that internal cavitation has not been observed in ODS alloys with coherent or fine nanodispersoids. On the contrary, micrographs from neutron- and ion-irradiated MA956 [298, 140] and neutron-irradiated EUROFER-ODS [299] appear to show evidence of nanodispersoid internal cavitation. A common factor in these alloys and the PM2000 of this study is that the nanodispersoids are relatively large (> 5 nm diameter) and therefore not likely to be fully coherent. Likewise, in MA957, the oxides that had internal cavities tended to be the large (> 10 nm diameter) pyrochlores that are likely to be semi-coherent [293]. And so, nanodispersoid coherency appears to be an important factor in limiting detrimental void growth, as it restricts internal cavitation of the oxides.

When the oxides are amorphized, an increase in volume is expected. However, the impact of this free volume increase on cavity formation is unclear. If the free volume in the oxides agglomerates, then formation of a critical nucleus for void development may be accelerated. For example, in amorphous germanium, a high density of small voids formed and then was shown to grow into large holes during ion irradiation [300]. By contrast, molecular dynamics simulations indicate that amorphous/crystalline interfaces may be effective at rapidly annihilating vacancies [301]. However, if there is insufficient relaxation, the increase in volume caused by amorphization could lead to strain at the oxide/matrix interface. Statics calculations suggest that an increase in misfit strain can enhance the sink strength of the crystalline nanodispersoids for interstitials [302]. Further research is needed though to understand how the sink strength at an amorphous/crystalline interface may differ.

Finally, it should be highlighted that helium generation is expected to be around 50 to 100 times greater for deuterium-tritium fusion than for fission [30]. Thus,

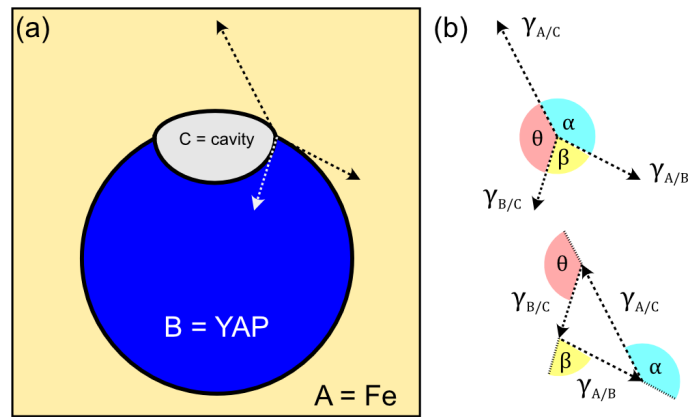


Figure 6.17: A schematic representation of a metal matrix, a nano-oxide particle, and a cavity in three-phase equilibrium. (a) Spatial map of the three phases A-Fe, B-YAP, and C-cavity showing the contact point (b) Neumann's triangle construction giving the balance of interfacial energies $\gamma_{A/C}$, $\gamma_{B/C}$, and $\gamma_{A/B}$ at the contact point. Here, α is the contact angle of the Fe, β is the contact angle of the YAP, and θ is the interior angle of the cavity.

at the low He production rates of this study, the formation of large voids rather than a high density of bubbles indicates a potential swelling concern for fusion applications. In addition, crystalline nanodispersoids have already been shown to readily trap helium and hydrogen [291, 303, 304]. An important question that requires further investigation, therefore, is whether amorphization of the oxides could cause unacceptably high levels of gas retention when ODS alloys are used as part of the first wall/blanket structure.

6.3 Conclusions

With the combination of damage observed in the nanodispersoids after neutron irradiation, including amorphization, cavitation, and new nanostructure formation, a dose dependent evolution is evident. At low doses, between 5.1 and 8.6 dpa, both the YAlO_3 perovskites in PM2000 and the $\text{Y}_2\text{Ti}_2\text{O}_7$ pyrochlores in MA957 were amorphized. In the case of the $\text{Y}_2\text{Ti}_2\text{O}_7$ pyrochlores, amorphization persisted up to 500°C even though ion irradiation experiments in literature suggest the critical amorphization temperature should be below $\sim 392 - 507^\circ\text{C}$. Given that the stability of pyrochlores increases as the radius ratio of the cations approaches unity, the ballistic mixing of undersized Fe atoms into the oxides is likely to be a destabilizing force. Although information on the factors influencing amorphization of YAlO_3 perovskite is sparse compared to the $\text{Y}_2\text{Ti}_2\text{O}_7$ pyrochlore, ballistic mixing is also likely to increase amorphization susceptibility, especially considering the highly endothermic reactions involved with accommodating Fe in the YAP structure when vacant cation sites are unavailable. Even after amorphization, the oxides continue to be subject to ballistic damage with irradiation. At high irradiation doses, > 50 dpa, the nanodispersoids have accumulated a significant volume fraction of ballistically injected Fe and Cr. The Fe and Cr atoms are able to re-agglomerate within the oxide and precipitate as crystalline islands.

Our results highlight that nanodispersoids may not be stable under irradiation, as has been frequently suggested in literature. Amorphization of the oxides alone is cause for concern when considering the application of ODS alloys to nuclear applications. First, it may either positively or negatively affect cavity swelling behavior by enhancing vacancy annihilation or by introducing additional strain at the interface that may significantly change the sink strength or the bias of the oxides. Second, for fusion first wall/blanket applications, the amorphization of the oxides raises questions on helium and tritium retention. Given the free volume associated with amorphous materials, there is a potential for these gases to be readily trapped inside the oxides. Finally, although not discussed extensively here, it is unknown how the mechanical properties of ODS alloys may be altered given the amorphization of the oxides. Since the oxides act as obstacles to dislocation and grain boundary motion, both low temperature strength and creep strength may be impacted.

At still higher doses, it is unclear how the oxides may continue to degrade. It is possible that the oxides will eventually break apart due to a high volume fraction of Fe-Cr rich islands, and form smaller oxides or nanoclusters. Given enough time under irradiation, a metastable particle size may be reached. The stability of the nanodispersoids after receiving lifetime doses anticipated for fusion and advanced fission applications thus warrants further investigation. Additional high resolution microscopy and APT work is also needed to examine the high-dose neutron irradiation response of oxides smaller than ~ 7 nm. APT studies frequently claim the small nano-oxides are sub-stoichiometric $\text{Y}_2\text{Ti}_2\text{O}_7$. Assuming this is true, their diffusivity and, by extension, their ability to recover from amorphization or ballistic mixing may be different. Thus, it needs to be verified whether the smallest oxides in MA957 are prone to a similar degradation process.

Chapter 7

Overall conclusions on phase stability in nuclear structural steels

Secondary phases and solute nanoclusters are critical to both the radiation resistance and the mechanical properties of nuclear structural steels. Nonetheless, there are many aspects of phase stability under irradiation where a fundamental understanding is lacking. These knowledge gaps are major limitations as the nuclear community looks to expand the applicability of materials such as austenitic stainless steels to new reactor concepts or to evaluate novel materials such as ODS alloys.

In this work, we address three questions regarding phase stability under irradiation that touch upon the variables of damage rate, temperature, and dose. First, the instability of Cu- and Ni-Si-Mn-enriched nano-clusters in a 304L austenitic stainless steel was investigated at high and low particle bombardment rates to evaluate the factors affecting ballistic dissolution susceptibility. Accelerated damage rate ion irradiations at 1×10^{-3} dpa/s were unable to fully simulate the solute nano-clustering observed after irradiation in the BOR60 reactor to 47.5 dpa at 9.4×10^{-7} dpa/s, 318 °C. In particular, Cu-enriched clusters that were radiation enhanced during neutron irradiation were ballistically dissolved, even when ion irradiations were

conducted between 62 and 102 °C higher. By contrast, radiation-induced Ni-Si-Mn-enriched clusters were able to nucleate into clusters matching the chemistry of G-phase with ion irradiations at 400 and 420 °C. At 380 °C, the evolution of Ni-Si-Mn-enriched clusters by ion irradiation was stagnated. The Heinig precipitate stability model was modified with solute-specific recoil rates to accurately predict the critical temperatures for a cluster to be stable at a given damage rate. The main parameters affecting cluster stability of the Cu- and Ni-Si-Mn-enriched clusters were related to the concentration profile near the cluster interface. This concentration profile provides the thermodynamic driving force for the restoring solute flux and is independent of irradiation. Thus, clusters containing different solute species may have innately different ballistic dissolution susceptibilities even under the same irradiation damage conditions. The modified Heinig model does not help predict steady-state precipitate microstructure, but can be used to identify temperature–damage rate operating conditions where precipitates are likely to be stable. While this may be useful to guide experimental design, it does not solve the key challenge associated with using accelerated damage rate irradiations as a surrogate for neutron irradiations: the temperature shifts required for precipitate stability are often prohibitively high for simulating other microstructural features such as dislocation loop or cavity microstructures.

The effect of temperature on phase stability was further explored in the context of radiation-induced hardening in neutron-irradiated ODS alloys. Vickers microhardness and uniaxial tensile tests of ODS alloys revealed that unlike RAFM steels that recover or soften at irradiation temperatures ≥ 400 °C, ODS alloys 12YWT, MA957, and PM2000 all exhibited some hardening up to 500 °C. This retained hardening is especially problematic considering the poor initial fracture toughness of ODS steels. Also, the considerable amount of hardening observed in the neutron-irradiated ODS alloys suggests that initial sink strength does not necessarily help suppress hardening phenomena. In neutron-irradiated PM2000, Cr-enriched clusters formed during irradiation at 287 to 500 °C while an Al-Ti enriched phase also precipitated at

500 °C. In neutron-irradiated MA957, both Cr- and Ni-Ti-enriched clusters nucleated over the same temperature range. By comparing the uniaxial tensile test results for MA957 to a comprehensive hardening model, it was revealed that the Cr-enriched clusters were the primary source of irradiation hardening. The results point to the potential importance of controlling the initial chemistry of ODS alloys and other nuclear structural steels. It is apparent that low Cr contents are needed to avoid Fe-Cr phase separation. Alternatively, higher operating temperatures may need to be considered for ODS alloys in fusion first wall/blanket designs. However, the RIS of Ti under neutron irradiation at 500 °C raises additional concerns over solute nanoclustering at higher temperatures. A further question is whether the RIS of Ti will affect the stability of the nano-oxides at higher irradiation doses, considering the coarsening resistance Ti promotes for oxides.

Finally, the destabilizing impact of high dose neutron irradiation on oxide particles was examined in PM2000 and MA957. While it has frequently been claimed in literature that oxides in ODS alloys are stable to high irradiation doses, our results show the dramatic evolution of the YAP and pyrochlore nanodispersoids in PM2000 and MA957, respectively. While initially crystalline, both the YAP and pyrochlore oxides were fully amorphized after irradiation at 335 °C after $\sim 5.1 - 5.5$ dpa. In addition, neutron irradiation resulted in amorphization of the oxide particles in MA957 up to 500 °C. As samples at higher irradiation temperatures were not available to examine, the critical amorphization temperatures relevant to the YAP and pyrochlore oxides under neutron irradiation are still unknown. Additional work is needed to establish these important values. Irradiation of pure YAP and pyrochlore samples may not be sufficient for such experiments, as our results suggest that ballistically injected Fe or Cr may increase the amorphization susceptibility of the oxides. An open question is the potential implications of oxide amorphization on ODS alloy performance. For fusion first wall/blanket applications, the trapping of tritium in the amorphous oxides is a key concern. Many of the nanodispersoids in PM2000 and MA957 irradiated to > 50 dpa had a large internal cavity. This

suggests that there is a notable amount of free volume in the amorphous oxides to accommodate tritium. Bias of the oxides for vacancies or interstitials may also be altered after amorphization. Assuming there is significant volume expansion when the particles are amorphized, there may be compressive stress at the interface so that vacancy capture becomes preferred. In fusion reactors, which are expected to have much more transmutation gas production than fission reactors, cavity swelling thus may be a concern.

At neutron irradiation doses > 50 dpa, a significant amount of Fe was ballistically mixed into the oxides. The accumulated Fe then formed crystalline islands in the amorphous oxides. It is unclear whether the oxides need to be amorphous for island formation to occur. Given the relatively consistent size of these islands, there may be a critical nucleus size for their precipitation. It is thus unclear whether internal crystalline islands can form in oxides $\lesssim 7$ nm in diameter. Examining the nanodispersoids at even higher doses would be valuable, as it is possible the large oxides may eventually disintegrate into several smaller oxides. Additionally, high dose data at 500°C and above is desired to illuminate whether the formation of crystalline islands within the oxides persists at high temperatures.

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Appendices

Appendix A

Neutron irradiation cycle histories

Table 1: Neutron irradiation history for the JP-26 experiment.

Cycle	Start Date	End Date	MWD	Accumulated MWD	Cycle Length (d)	Cooling Period (d)
398	12/11/2003 02:36	01/06/2004 18:20	2186.50	2186.50	26.66	27.87
399a	02/03/2004 15:08	02/16/2004 13:53	0.00	2186.50	12.95	13.80
399b	03/01/2004 09:00	03/14/2004 14:39	2164.60	4351.10	13.24	43.91
400	04/27/2004 12:31	05/21/2004 17:35	2068.42	6419.52	24.21	55.18
401	07/15/2004 21:52	08/09/2004 07:37	2086.90	8506.42	24.41	50.17
402a	09/28/2004 11:40	10/08/2004 20:10	853.69	9360.11	10.35	32.81
402b	11/10/2004 15:41	11/23/2004 15:27	1956.86	11316.97	12.99	—

Table 2: Neutron irradiation history for the JP-29 experiment

Cycle	Start Date	End Date	MWD	Accumulated MWD	Cycle Length (d)	Cooling Period (d)
403a	01/26/05 11:56	01/26/05 12:52	0.00	0.00	0.04	0.04
403b	01/26/05 13:43	02/04/05 15:35	777.93	777.93	9.08	61.17
404	04/06/05 19:43	04/30/05 00:05	1967.07	2745.00	23.18	5.57
403c	05/05/05 13:43	05/18/05 22:01	1898.61	4643.61	13.35	8.90
405	05/27/05 19:43	06/20/05 01:04	1973.56	6617.17	23.22	8.03
406a	06/28/05 01:50	07/08/05 23:52	0.00	6617.17	10.92	3.34
406b	07/12/05 07:58	07/23/05 16:15	1888.75	8505.92	11.35	143.85
407a	12/14/05 12:37	12/14/05 12:39	0.01	8505.93	0.00	6.84

Table 2 continued

Cycle	Start Date	End Date	MWD	Accumulated MWD	Cycle Length (d)	Cooling Period (d)
407b	12/21/05 08:50	01/13/06 21:08	1977.56	10483.49	23.51	529.46
409	06/27/07 08:05	07/20/07 16:00	1979.59	12463.08	23.33	25.67
410a	08/15/07 08:06	09/03/07 12:00	1626.66	14089.74	19.16	22.81
410b	09/26/07 07:32	09/26/07 13:10	4.59	14094.33	0.23	1.64
410c	09/28/07 04:34	10/02/07 13:42	355.58	14449.91	4.38	42.74
411	11/14/07 07:31	12/08/07 00:43	2003.52	16453.43	23.72	10.39
412	12/18/07 10:09	01/11/08 02:00	2008.23	18461.66	23.66	26.32
413	02/06/08 09:35	03/01/08 09:00	2025.60	20487.26	23.98	24.96
414a	03/26/08 08:09	03/26/08 08:20	0.00	20487.26	0.01	0.16
414b	03/26/08 12:10	04/19/08 14:14	2046.33	22533.59	24.09	45.31
415a	06/03/08 21:35	06/21/08 21:06	0.00	22533.59	17.98	4.47
415b	06/26/08 08:18	06/30/08 05:25	1993.10	24526.69	3.88	16.11
416	07/16/08 08:02	08/06/08 10:46	1813.65	26340.34	21.11	48.88
417	09/24/08 07:46	10/18/08 06:50	2021.37	28361.71	23.96	25.05
418	11/12/08 08:01	12/05/08 19:30	1994.78	30356.49	23.48	32.19
419	01/07/09 00:00	01/31/09 11:55	2046.71	32403.20	24.50	17.84
420	02/18/09 08:10	03/14/09 20:00	2072.12	34475.32	24.49	59.51
421	05/13/09 08:21	06/06/09 18:52	2070.08	36545.40	24.44	17.54
422	06/24/09 07:56	07/18/09 02:10	2011.81	38557.21	23.76	18.19
423	08/05/09 06:42	08/29/09 14:01	2057.18	40614.39	24.30	45.68
424a	10/14/09 06:14	10/31/09 03:00	1424.37	42038.76	16.87	2.49
424b	11/02/09 14:40	11/09/09 17:36	2027.14	44065.90	7.12	15.72
425a	11/25/09 10:46	11/30/09 14:19	433.07	44498.97	5.15	3.03
425b	12/03/09 15:00	12/21/09 13:35	2040.27	46539.24	17.94	15.76
426	01/06/10 07:52	01/30/10 11:00	2048.95	48588.19	24.13	19.91
427	02/19/10 08:55	03/15/10 08:03	2033.72	50621.91	23.96	50.88
428	05/05/10 05:15	05/29/10 08:35	2041.49	52663.41	24.14	17.89
429	06/16/10 05:54	07/10/10 10:00	2044.36	54707.76	24.17	17.80
430	07/28/10 05:14	08/21/10 13:00	2057.32	56765.09	24.32	52.88
431	10/13/10 10:14	11/08/10 05:00	2193.51	58958.60	25.78	14.13
432	11/22/10 08:11	12/18/10 05:00	2194.80	61153.40	25.87	23.11
433	01/10/11 07:45	02/05/11 10:49	2217.60	63371.00	26.13	15.77
434	02/21/11 05:12	03/19/11 08:00	2207.37	65578.37	26.12	43.93
435	05/02/11 06:22	05/25/11 14:00	1973.37	67551.74	23.32	18.75
436a	06/13/11 08:05	06/27/11 17:30	1218.01	68769.75	14.39	2.59
436b	06/30/11 07:33	07/11/11 08:00	2138.91	70908.66	11.02	20.91
437	08/01/11 05:50	08/26/11 23:29	2167.63	73076.29	25.74	44.29
438	10/10/11 06:26	11/05/11 01:55	2189.59	75265.88	25.81	16.17
439	11/21/11 05:55	12/16/11 21:43	2171.77	77437.65	25.66	23.43
440a	01/09/12 08:08	01/10/12 10:01	90.14	77527.79	1.08	75.85
440b	03/26/12 06:19	04/19/12 00:00	2094.63	79622.42	23.74	18.26

Table 2 continued

Cycle	Start Date	End Date	MWD	Accumulated MWD	Cycle Length (d)	Cooling Period (d)
441	05/07/12 06:16	05/31/12 22:25	2097.33	81719.75	24.67	17.41
442	06/18/12 08:15	07/13/12 06:46	2117.12	83836.87	24.94	17.96
443	07/31/12 05:50	08/24/12 19:10	2068.59	85905.46	24.56	45.45
444	10/09/12 05:59	11/03/12 16:10	2148.68	88054.14	25.42	16.64
445	11/20/12 07:37	12/15/12 16:54	2150.77	90204.91	25.39	23.62
446	01/08/13 07:49	02/02/13 07:49	2125.94	92330.85	25.00	93.94
447	05/07/13 06:17	06/01/13 12:51	2143.58	94474.43	25.27	16.79
448	06/18/13 07:44	07/13/13 14:11	2147.63	96622.06	25.27	—

Table 3: Neutron irradiation history for the BORIS 6 and 7 experiments.

Cycle	Start Date	End Date	MWD	Accumulated MWD	Cycle Length (d)	Cooling Period (d)
73	6/26/2001	8/12/2001	1958.96	1958.96	47	9
73a	8/21/2001	10/21/2001	2652.08	4611.04	61	84
74	1/13/2002	2/26/2002	1543.75	6154.79	44	15
74a	3/13/2002	5/12/2002	2633.21	8788.00	60	47
75	6/28/2002	8/7/2002	1667.71	10455.71	40	13
75a	8/20/2002	10/15/2002	2847.50	13303.21	56	41
76	11/25/2002	1/15/2003	2567.13	15870.33	51	27
76a	2/11/2003	3/10/2003	1385.08	17255.42	27	10
76b	3/20/2003	5/11/2003	2393.42	19648.83	52	46
77	6/26/2003	8/16/2003	2286.88	21935.71	51	16
77a	9/1/2003	10/12/2003	1955.88	23891.58	41	43
78	11/24/2003	1/12/2004	2198.04	26089.63	49	11
78a	1/23/2004	3/14/2004	2546.58	28636.21	51	10
78b	3/24/2004	5/23/2004	3053.50	31689.71	60	—

Appendix B

Mass-to-charge spectrum ranges

Table 4: Ranges used to label the AuSS mass-to-charge spectrum.

Peak m/z (Da)	Lower m/z (Da)	Upper m/z (Da)	Ion	Peak m/z (Da)	Lower m/z (Da)	Upper m/z (Da)	Ion
6.0	5.8700	6.2630	C ²⁺	32.3	32.2450	32.3440	Mo ³⁺
10.3	10.1140	10.5290	P ³⁺	32.5	32.4080	32.5270	Cu ²⁺
12.0	11.8390	12.1670	C ⁺	32.7	32.5640	32.6890	Mo ³⁺
14.0	13.8752	14.3084	Si ²⁺	33.0	32.9010	33.0420	CrN ²⁺
14.5	14.3730	14.6350	Si ²⁺	33.3	33.2110	33.3920	Mo ³⁺
15.0	14.8310	15.2030	Si ²⁺	34.0	33.8820	34.0590	CrO ²⁺
15.5	15.3120	15.6390	P ²⁺	34.5	34.3420	34.5790	Ga ²⁺
18.0	17.8600	18.1440	H ₂ O ⁺	36.0	35.8790	36.0560	FeO ²⁺
24.0	23.8520	24.2010	C ₂ ⁺	46.0	45.8370	46.0340	Mo ²⁺
25.0	24.8240	25.2190	Cr ²⁺	47.0	46.8370	47.0410	Mo ²⁺
25.5	25.3320	25.6320	V ²⁺	47.5	47.3560	47.5630	Mo ²⁺
26.0	25.8200	26.2900	Cr ²⁺	48.0	47.7800	48.0540	Mo ²⁺
26.5	26.4030	26.7410	Cr ²⁺	48.5	48.3120	48.5690	Mo ²⁺
27.0	26.8580	27.1440	Fe ²⁺	49.0	48.7630	49.1120	Mo ²⁺
27.5	27.3420	27.6990	Mn ²⁺	50.0	49.8640	50.0000	Mo ²⁺
28.0	27.8483	28.2910	Fe ²⁺	53.0	52.7720	53.1240	MoN ²⁺
28.5	28.3380	28.7330	Fe ²⁺	54.0	53.7340	54.0870	MoN ²⁺
29.0	28.8080	29.2210	Ni ²⁺	54.5	54.2800	54.5040	MoN ²⁺
29.5	29.3150	29.6350	Co ²⁺	55.0	54.6650	55.1140	MoN ²⁺
30.0	29.8410	30.2170	Ni ²⁺	55.5	55.3060	55.5630	MoN ²⁺
30.5	30.3370	30.6010	Ni ²⁺	56.0	55.7230	56.1410	MoN ²⁺
31.0	30.8000	31.1750	Ni ²⁺	57.0	56.6220	57.0710	MoN ²⁺
31.3	31.2320	31.3370	Mo ³⁺	58.0	57.6580	58.2600	Ni ⁺
31.5	31.3820	31.5610	Cu ²⁺	59.0	59.6460	60.1690	Ni ⁺
31.7	31.5680	31.6760	Mo ³⁺	63.0	62.5880	63.3100	Cu ⁺
32.0	31.8140	32.1530	Ni ²⁺	65.0	64.5270	65.2480	Cu ⁺
				69.0	68.6750	69.2160	Ga ⁺

Table 5: Ions assignments for each peak in the MA957 mass-to-charge spectra

Peak m/z (Da)	Ion	Peak m/z (Da)	Ion
5.5	B ²⁺	29.5	Co ²⁺
6	C ²⁺	29.7	Y ³⁺
7	N ²⁺	30	Ni ²⁺
9	Al ³⁺	30.5	Ni ²⁺
11	B ⁺	30.7	Mo ³⁺
12	C ⁺	31	TiO ²⁺
13.5	Al ²⁺	31.3	Mo ³⁺
14	Si ²⁺	31.5	TiO ²⁺
14.5	Si ²⁺	31.7	Mo ³⁺
15.3	Ti ³⁺	32	TiO ²⁺
15.5	P ²⁺	32.3	Mo ³⁺
15.7	Ti ³⁺	32.5	TiO ²⁺
16	O +	32.7	Mo ³⁺
16.3	Ti ³⁺	33	TiO ²⁺
16.7	Ti ³⁺	33.3	Mo ³⁺
21.5	AlO ²⁺	34	CrO ²⁺
23	Ti ²⁺	44	FeO ₂ ²⁺
23.5	Ti ²⁺	46	Mo ²⁺
24	Ti ²⁺	46.5	Nb ²⁺
24.5	Ti ²⁺	47	Mo ²⁺
25	Cr ²⁺	47.5	Mo ²⁺
25.5	V ²⁺	48	Mo ²⁺
26	Cr ²⁺	48.5	Mo ²⁺
26.5	Cr ²⁺	49	Mo ²⁺
27	Fe ²⁺	50	Mo ²⁺
27.5	Mn ²⁺	52.5	YO ²⁺
28	Fe ²⁺	53	MoN ⁺²
28.5	Fe ²⁺	54.5	MoN ⁺²
29	Ni ²⁺	69	Ga ⁺

Table 6: Isotopic abundance matrix for ZQ21

m/z	Ion								
	B ²⁺	C ²⁺	N ²⁺	A ₁ ³⁺	P ³⁺	B ⁺	C ⁺	Al ²⁺	Si ²⁺
5.5	1								
6.0		0.89073							
7.0		0.09811	0.99474						
9.0				1					
10.3					0.99970				
11						1			
12							0.89073		
13.5								1	
14.0							0.09811		0.92009
14.5									0.04928
15.0									0.03064

	N ⁺	Ti ³⁺	O ⁺	Ti ²⁺	C ₂ ⁺	Cr ²⁺	V ²⁺	Al ⁺
14.0	0.99474							
15.0	0.00526							
15.3		0.08154						
15.7		0.07299						
16.0		0.63006	0.99762					
16.3		0.15985						
16.7		0.05556						
23.0				0.08154				
23.5				0.07299				
24.0				0.63006	0.79340			
24.5				0.15985			0.00001	
25.0				0.05556		0.03256	0.00103	
25.5						0.00121	0.99896	
26.0					0.17478	0.83271		
26.5						0.07858		
27.0						0.05495		1
27.5								
28.0					0.00963			

Table 6 continued

m/z	Ion							
	Mn ²⁺	Fe ²⁺	Ni ²⁺	Co ²⁺	Y ³⁺	Mo ³⁺	TiO ²⁺	O ₂ ⁺
26.5	0.00019							
27.0	0.02060	0.05593						
27.5	0.97888	0.00194						
28.0	0.00034	0.87333						
28.5		0.06397		0.00008				
29.0		0.00481	0.62397	0.00029				
29.5		0.00002	0.02616	0.75274				
29.7					0.99924			
30.0			0.27598	0.24689	0.00074			
30.5			0.02568	0.00001				
30.7						0.14836		
31.0			0.02842			0.00037	0.08135	
31.3						0.09205		
31.5			0.00695				0.07281	
31.7						0.11078		
32.0			0.01284			0.21201	0.62856	0.99524
32.3						0.09533		
32.5							0.15946	
32.7						0.24525		
33.0						0.00008		0.05543
33.3						0.09576		

Table 6 continued

m/z	Ion							
	CrO ²⁺	Ga ²⁺	Mo ²⁺	Nb ²⁺	YO ²⁺	MoN ²⁺	Fe ⁺	Ga ⁺
33.0	0.03248							
34.0	0.83072							
34.5	0.07840	1						
46.0			0.14836	0.00002				
46.5			0.00037	0.97185				
47.0			0.09205	0.02686				
47.5			0.11078	0.00126				
48.0			0.21201					
48.5			0.09533					
49.0			0.24525					
50.0			0.09576					
52.5					0.99686			
53.0					0.00074	0.14758		
54.5						0.11069		
56.0						0.24446	0.87333	
69.0								1

Vita

Samara Levine was born and raised in the U.S.A. on Long Island in New York. She attended Virginia Tech from 2009 to 2013, earning a Bachelor of Science in Materials Science and Engineering. Subsequently, she was a nuclear engineer for Newport News Shipbuilding, where she worked on reactor plant construction for the U.S.S. Gerald R. Ford aircraft carrier and temporary systems for the S8G and MARF submarine prototypes. In 2016, she returned to school to study irradiation damage in nuclear structural materials. She attended the University of Michigan in Ann Arbor, and was awarded a Nuclear Engineering University Program fellowship by the U.S. Department of Energy. Her research, under the supervision of Dr. Gary Was, involved working with BOR-60 neutron-irradiated austenitic stainless steels to understand the influence of previous irradiation history on subsequent microstructure development by ion irradiations. After completing a Master of Science in Nuclear Engineering and Radiological Sciences in 2019, she transferred to the University of Tennessee to continue towards a Ph.D. degree, under the supervision of Dr. Steven Zinkle. For two years she was awarded the Graduate Advancement Training and Education fellowship by the University of Tennessee Science Alliance as she worked closely with the fusion materials program at Oak Ridge National Laboratory, examining ferritic oxide dispersion strengthened steels that were irradiated in the High Flux Isotope Reactor. Her focus has been on understanding the fundamental mechanisms causing nanodispersoid instabilities and phase instabilities in the matrix during irradiation.