# Journal Pre-proof

## Atom Probe Tomography Characterization of High-Dose Ion Irradiated MA957

Jing Wang , Mychailo B. Toloczko , Victor N. Voyevodin ,
Viktor V. Bryk , Oleg V. Borodin , Valentyn V. Mel'nychenko ,
Alexandr S. Kalchenko , Frank A. Garner , Lin Shao

Please cite this article as: Jing Wang , Mychailo B. Toloczko , Victor N. Voyevodin , Viktor V. Bryk ,
Oleg V. Borodin , Valentyn V. Mel'nychenko , Alexandr S. Kalchenko , Frank A. Garner , Lin Shao ,
Atom Probe Tomography Characterization of High-Dose Ion Irradiated MA957, *Journal of Nuclear
Materials* (2020), doi: https://doi.org/10.1016/j.jnucmat.2020.152528

Atom Probe Tomography Characterization of High-Dose Ion Irradiated MA957

Jing Wang[a], Mychailo B. Toloczko[a,*], Victor N. Voyevodin[b], Viktor V. Bryk[b], Oleg V. Borodin[b], Valentyn V. Mel'nychenko[b], Alexandr S. Kalchenko[b], Frank A. Garner[c], Lin Shao[c]

[a]Pacific Northwest National Laboratory, Richland, MS J4-55, 902 Battelle Blvd, WA, 99354, USA

[b]Kharkov Institute of Physics and Technology, Kharkov, Ukraine

[c]Texas A&M University, College Station, TX, 77840, USA

*Corresponding author. mychailo.toloczko@pnnl.gov,

Abstract

Because the microstructure of oxide dispersion strengthened (ODS) alloys largely determines its mechanical properties in nuclear reactors, it is critical to understand the irradiation response of microstructure after high-dose radiation damage for safety and performance concerns. This paper presents a comprehensive characterization of microstructural responses to ion irradiation of the ODS ferritic alloy MA957 using atom probe tomography and compares the observations to current theories on mechanisms for microstructural evolution during irradiation. The MA957 specimens were irradiated by 1.8 MeV $Cr^{3+}$ ions to doses and at temperatures relevant to advanced fast reactors (100 dpa and 500 dpa at 400–500 °C). The stability of YTiO particles, formation of alpha prime.($\alpha'$), and radiation-induced segregation were quantified and analyzed. The results show that the evolution of YTiO particles with respect to dose and temperature is consistent with the Nelson-Hudson-Mazey rate theory model that considers the competing effects of recombination and ballistic dissolution. The formation of Cr-rich precipitates ($\alpha'$) was observed in specimens irradiated at temperatures up to 450 °C, and it shows a strong dependence on temperature. Irradiation-induced segregation on grain boundaries was investigated in 100 dpa specimens. In addition to the commonly studied element Cr, this study also analyzed segregation of Y and Ti. While the magnitude of segregation varies due to intrinsic variability of grain boundary character, a clear trend with respect to irradiation temperature can be observed. Overall, these results revealed relatively small but distinct effects of irradiation on microstructure evolution to 100 or 500 dpa, demonstrating the excellent radiation tolerance of ODS alloys.

Keywords

Oxide dispersion strengthened (ODS) alloy; Irradiation; Atom probe tomography (APT); Radiation-induced precipitation (RIP); Radiation-induced segregation (RIS)

1

## Introduction

Some advanced reactor concepts require core materials to operate at peak temperatures above 600 °C near the top of the core while also sustaining peak radiation damage up to 500 displacements per atom (dpa) at locations closer to the core center [1, 2]. Oxide dispersion strengthened (ODS) ferritic alloys are considered promising candidates for reactor cladding and possibly subassembly ducts, in advanced fast reactors because they have significantly better high temperature strength and creep resistance than conventional ferritic/martensitic steels [2, 3]. The dispersion of nanometer-scale, thermally stable oxide particles not only improves tensile and creep resistance by providing barriers to dislocation motion, but likely also leads to enhanced radiation damage tolerance by providing additional sinks and sites for point defect recombination [2, 4]. Thus, understanding the stability of oxide particles under high-dose irradiation is a key factor in evaluating long-term reliability and safety of ODS ferritic alloys. It is currently impractical to achieve substantial doses using neutrons, and thus many current studies, including this one, use ion irradiations. The focus of this paper is to provide a comprehensive analysis of microstructure evolution in a systematic, high-dose, ion-irradiation study and to compare the observations to current theories on mechanisms for microstructural evolution during irradiation. This information is needed to make initial estimates of high-dose neutron irradiation microstructure stability and associated mechanical property changes of ODS ferritic alloys.

The lifetime of reactor structures depends on the mechanical, physical, and corrosion behavior of materials. Microstructure studies are performed to aid in understanding the evolution of those properties, to either improve existing materials or design new materials. In the absence of the ability to perform a material property test, quantification of microstructure features can also be used to estimate material properties, such as estimating yield strength changes in irradiated materials [5-8]. The aim of this work is to add to the knowledge base of irradiation effects on ODS ferritic alloys for these purposes.

At present, there are a limited number of studies of irradiation effects on ODS ferritic alloys at high doses (near or above 100 dpa), which is needed for some fast reactor concepts. Most of them were conducted on MA957 in fast reactors, namely, JOYO (Japan) [9-11], Phénix (France) [12-14], and the Fast Flux Test Facility (FFTF) (US) [3, 15, 16]. These studies focused on the mechanical properties, (such as tensile, hardness, and creep strength), and microstructure, (such as oxide particle phase stability and void swelling). Overall, the results from these tests suggest that YTiO particles readily survive to ~100 dpa, therefor providing excellent swelling and creep resistance, although some conflicting results on microstructure response under specific conditions have been reported. Bailey et al. [16] studied MA957 irradiated at FFTF from 412 °C to 670 °C; they found significant oxide particle size reduction at 412 °C, while at higher temperatures, oxide particle sizes converged to unirradiated condition. In studies by Ribis et al. [12, 13], oxide particle sizes were found almost unchanged after irradiation at 412 °C and 430 °C to 50–75 dpa in Phénix. These discrepancies are tentatively attributed to differences in the characterization techniques, i.e., atom probe tomography

(APT) vs. transmission electron microscopy (TEM); however, correlation studies using the same materials suggest such differences are usually small [17]. Due to complications in the materials fabrication process and in-reactor conditions, these neutron irradiation data alone, although valuable, are not sufficiently systematic to establish a clear, more quantitative trend to estimate higher dose response.

High-dose ion irradiation data [8, 18-28] are more readily available than data for neutron irradiation. The overall trend of YTiO particle stability agrees with results of neutron irradiations, but similarly, conflicting results have also been reported. Certain et al. performed a temperature dependence study from −75 to 600 °C on 14YWT and observed significant dissolution of oxide particles to almost undetectable sizes, at −75 °C [23]. Size distributions of oxide particles at higher temperatures were similar to those of unirradiated samples. However, Lescoat et al. reported coarsening of YTiO particles in a Fe-18Cr ODS ferritic alloy irradiated by 500 keV self-ions at 500 °C up to 150 dpa [29]. Aydogan et al. investigated dose dependence of oxide particles in 14YWT at 450 °C using TEM and APT [28]; oxide particle size reduction and number density increase continued to ~585 dpa. Chen et al., on the other hand, found no obvious particle size change in a 12Cr ferritic/martensitic ODS alloy irradiated to ~800 peak dpa at 475 °C [25]. The differences in observations may be caused by many factors, from intrinsic materials variations to ion irradiation parameters. This investigation does not aim to resolve these discrepancies, but rather to provide a set of systematic, well-characterized data and discuss the observations in the context of known models for the community to consider and use.

So far, most microstructural analysis of ODS ferritic alloys has focused on the stability of the oxide particles; however, other irradiation-induced microstructural alterations, such as second-phase precipitates, matrix composition, and grain boundary chemistry, must be characterized to more fully investigate potential correlations with mechanical properties. Current ODS ferritic alloys have Cr content ranging from 9 to 20 wt%; thus, many ODS alloys with >9 wt% Cr fall within the range where alpha prime (α′) can form during irradiation [30, 31]. The formation of α′ precipitates in non-ODS Fe-Cr systems has often been attributed to being the primary cause of the so-called "475 °C embrittlement," where Fe-Cr alloys exhibited a significant increase in brittleness after thermal aging at 475 °C [32, 33]. Some studies have demonstrated that this embrittlement can occur in high-Cr ODS alloys via thermal aging as well [34]. Irradiation is known to enable the formation of α′ in Fe-Cr alloys under conditions where thermal aging will not [35, 36]. Therefore, a systematic characterization of the formation and evolution of α′ is necessary.

Grain boundary segregation is less studied in ODS ferritic alloys, probably because ODS ferritic alloys usually retain their ductility to a reasonable extent after irradiation, and there is no indication of intergranular failure as the main failure mode [37-39]. Recent studies on the development of a new nanostructured ODS alloy show that grain boundary decohesion could be a

primary failure mode in these materials [40-42]. Studies of radiation-induced segregation (RIS) on grain boundaries usually offer conflicting results, and a systematic investigation is difficult because it depends on the types of grain boundaries, and the exact mechanisms are not yet clear [43-45].

## Experimental

### Materials

For this study, specimens of MA957 (Fe-14Cr-1Ti-3Mo-0.25$Y_2O_3$) were retrieved from archival, unirradiated material (heat DBB0111, tube ID EV). MA957 is an early ODS alloy that was originally purchased from the International Nickel Company for the U.S. Liquid Metal Fast Breeder Reactor program decades ago. The material used for this study was originally fabricated into pressurized tubes to study neutron irradiation-induced creep response [3]. Some of these MA957 tubes were irradiated in the Materials Open Test Assembly at FFTF. A brief description of the fabrication procedure was described in the irradiation creep study [3] while more detailed fabrication procedures were described in detail in several previous reports to the U.S. Department of Energy [46, 47]. The nominal composition of the heat used in this study is listed in Table 1. A prior TEM-based study of the ion irradiated specimens revealed a steady increase in swelling between 100 dpa and 500 dpa, with a maximum of 4.5% swelling after 500 dpa at 450 °C [48].

### Ion Irradiation

The MA957 samples were cut from unirradiated pressurized tube specimens into 3 mm diameter TEM disk size specimens using electric discharge machining. For purposes of ion irradiation, the specimens were mechanically polished to a 1 μm surface finish, followed by final finishing with colloidal silica. The polished specimens were irradiated with 1.8 MeV $Cr^{3+}$ ions (dose rate on the order of $1 \times 10^{-2}$ dpa/s) to 100 dpa and 500 dpa at 400, 420, 450, and 500 °C at the Kharkov Institute of Physics (KIPT). The irradiation temperature range is of interest because it is highly relevant to fast reactor core materials. The dose was calculated at the examination depth, which is ~100–200 nm below the irradiated specimen surface, using the Kinchin-Pease method in the Stopping and Range of Ions in Matter (SRIM) software [49, 50]. The depth of interest was selected as a compromise between surface effects and injected interstitials based on past studies and experience [25, 51, 52]. However, SRIM only estimates ion range using the Monte Carlo method rather than modeling the prolonged ion irradiation process, where the target materials may undergo microstructural changes such as sputtering and diffusion.

A previous study found that sputtering alone could play a noticeable role in altering dose and ion distribution profiles at 500 dpa [53]. Comparisons of SRIM-calculated and sputtering-compensated

4

dose and injected ion profiles for the present work are shown in Figure 1. Considering only surface sputtering, the estimated dose changed from 500 to ~569 dpa (a ~14% difference) within the 100–200 nm range. The injected ion profile moved closer to the surface due to sputtering, and the adjusted injected ion concentration at the examined depth is ~1.7%, compared to 0.7% estimated by SRIM. Note that solute diffusion was not considered in this calculation. A helpful discussion of the effects of diffusion can be found in Doyle et al. [54].

Another undesired artifact in ion irradiation is possible carbon contamination. Previous studies have suggested that it could adversely affect the microstructural evolution of the target material [55-57] and mechanical properties such as microhardness [58]. In the present study, post-irradiation composition analysis using procedures stated in Wang et al. [55] confirmed that carbon concentration in the specimen is indistinguishable from that of unirradiated specimens. KIPT has implemented procedures to maintain good vacuum cleanliness to prevent carbon contamination.

**Atom Probe Tomography**

APT specimens were prepared using an FEI Quanta dual-beam focused ion beam (FIB) scanning electron microscope following a standard lift-out procedure [59]. The position of the needle was actively tracked during fabrication, and the orientation of the tip was parallel to the ion irradiation incident direction. All finished needles were cleaned using a final mill with a low energy ion beam (2–5 keV) to remove potential gallium contamination. In general, 3–9 APT needles were prepared for each condition. APT data were then acquired using a CAMECA Local Electrode Atom Probe (LEAP) 4000X HR in laser pulsing mode at the Environmental Molecular Sciences Laboratory at Pacific Northwest National Laboratory (PNNL). Typical operating parameters were a pulse repetition rate of 200 kHz, an evaporation rate of 0.3% (0.003 detected ions/pulse), a specimen temperature set at 40 K, and a laser ($\lambda$ = 355 nm) energy of 60 pJ. The obtained data were reconstructed using the Integrated Visualization and Analysis Software (IVAS), version 3.6. A summary that lists all APT needles is displayed in Table 2. It is worth noting that APT needles from 500 dpa specimens failed prematurely more frequently during APT data collections than 100 dpa counterparts. Therefore, fewer APT data sets were collected in a single FIB lift-out. APT needles for specimens irradiated at 450 °C and 500 dpa experienced a nearly 50% failure rate during data acquisition because high void swelling weakened them [48].

Solute clusters, i.e., YTiO particles and α' precipitates, in specimens were identified using the isoconcentration surface method [60]. Particle diameters were calculated assuming the volume enclosed by the isoconcentration surface is spherical. For number density calculation, particles that intersected the edge of the analysis volume in each data set were considered to contribute half instead of one. The size distributions were generated using only fully enclosed clusters (those that

5

did not intersect with the data-set edge) to avoid errors in measuring partially enclosed ones. Note that there is no perfect cluster analysis for APT data; we choose isoconcentration surface because it is simple, intuitive, and produces good enough quality results. A brief comparison of the results from the isoconcentration surface method and the density-based method in an ODS alloy can be found in one of our previous studies [61]. Grain boundary chemistry was analyzed using 1D concentration profiles. A typical region of interest is defined by a bounding box of size $20 \times 20 \times 20$ nm$^3$. The 1D profiles were then generated in directions perpendicular to the grain boundary plane with a fixed interval of distances. Because the existence of α' precipitates in some conditions may perturb the concentration profile measurement, all identified Cr-rich α' precipitates were removed from APT data sets before measuring Cr concentration. There is, however, an intrinsic limitation on investigating grain boundary chemistry in ODS alloys using APT. In the current study, resolving the exact grain boundary type is challenging, since extraction of crystallographic information from APT data is difficult. Although grain boundary type can be determined in materials systems like aluminum alloys, we found the technique challenging to transfer to steel systems [62, 63].

## Results

### YTiO Particles

Snapshots of typical APT reconstructions for unirradiated and 100 dpa specimens are displayed in Figure 2. YTiO particles maintained a visually noticeable presence in the entire temperature range, and a couple of YTiO particles significantly larger than the rest were often captured in the analysis volume. Distributions of Y, TiO, and YO ions are strongly correlated and are considered good indicators of YTiO oxide particles. Elemental Ti exhibited slightly higher concentration in the particles than in the matrix, but it was not distinct enough to be a meaningful indicator for smaller clusters. O is also associated with YTiO particles, but its distribution is more diffuse, making its boundary hard to define even for large particles. Grain boundary segregation of displayed ions in these figures clearly shows some distinctions at different temperatures; detailed results will be presented in the grain boundary chemistry section.

Figure 2. Ion maps of Ti, Y, O, TiO, and YO for typical ion-irradiated and unirradiated MA957 APT specimens: (a) 400 °C, 100 dpa; (b) 420 °C, 100 dpa; (c) 450 °C, 100 dpa; (d) 500 °C, 100 dpa; and (e) unirradiated.

Figure 3 shows the size distributions of YTiO particles in unirradiated and ion-irradiated MA957. Note that the *y*-axis in each size distribution plot is the number density of particles in each bin. The sum over all bins is the overall number density of particles in the test material. The plots show that the majority of oxide particle sizes fall within 0.5–10 nm in diameter before and after irradiation, and the size distribution shape is affected by irradiation conditions. In unirradiated specimens, the size distribution follows a Gaussian-like profile with a minor tail extending to larger sizes. After lower-temperature irradiation, below 450 °C and especially at 400 °C, the size distributions

deviated from a Gaussian-like distribution and became significantly positively skewed towards a greater proportion of smaller sizes appeared. The higher proportion of smaller particles suggests that YTiO particles experienced refinement and suffered a loss of solute atoms during irradiation. At 500 °C, the size distribution retained a shape similar to that of unirradiated MA957. When irradiated at 400 °C and 420 °C, increasing the damage level from 100 to 500 dpa caused a further increase in number density and a reduction in size. At 450 °C and 500 °C, size distributions of oxide particles were similar in 100 dpa and 500 dpa specimens.

The statistical values for particle diameter and the number density of YTiO particles are summarized in Figure 4 and Table 3. When irradiated at 400 °C, the average sizes of oxide particles shrank to 3.40 nm at 100 dpa and further down to 2.92 nm at 500 dpa. At 500 °C, the average oxide particle size was 4.14 nm at 100 dpa, which is only ~5% smaller than particles in unirradiated specimens. Even at 500 dpa, the average particle experienced a mere ~12% reduction to 3.87 nm. The evolution of average sizes suggests that YTiO particles were partially dissolved at lower irradiation temperatures, but less so at higher temperatures. The estimated 95% confidence intervals for the average particle size are extremely small for all conditions, suggesting that a few hundred particle measurements will result in a fairly accurate mean value. In other words, although average particle sizes may fall within the standard deviation range of samples of other irradiation conditions, the trend observed for the mean diameter is likely accurate.

The statistical confidence intervals in the number density are wide, making it more difficult to identify statistically significant trends in number density. Obtaining tight confidence intervals for number density is more difficult than for YTiO particle size because particle size is measured on the per-particle basis while the number density is measured on the per-meaningful-volume basis. In this study, number density was measured per APT specimen, which contains at least dozens of YTiO particles. Considering that measured standard deviations for number density are still noticeable and the number of samples is smaller, confidence interval thus cannot achieve the tightness of the particle size. A quick, semi-quantitative statistical analysis demonstrates this. Assuming number density follows a normal distribution, the minimal number of unit volumes, $n$, to reach a certain confidence level is $n = 4z^2\sigma^2 / W^2$, where $z$ is the standard $z$-score (1.96 for 95% confidence), $\sigma$ is standard deviation of the population, and $W$ is twice the margin of error. In number density measurements, $n$ is typically given as the number of different volumes that are examined. As an example, assume we would like to reach a margin of error of no greater than $0.25 \times 10^{23}$ m$^{-3}$ (~10% of mean number density in unirradiated specimens). If $\sigma$ is assumed to be $1 \times 10^{23}$ m$^{-3}$, the minimum number of surveyed volumes per condition would be 62. This is likely well beyond the scope of most known studies of microstructures. In our study, we tried our best to ensure good statistics by examining 3–9 APT specimens per condition with most conditions having 5 or more

7

tips, and the corresponding margins of error are similar to the standard deviation values, except for cases where only three or four individual APT specimens were available.

For YTiO particles irradiated to 100 dpa, there is an apparent trend for the number density to be lower than the unirradiated value, especially at 400°C where it is half the unirradiated value, but given the wide confidence intervals for mean value of number density, it can only safely be said that YTiO particles irradiated to 100 dpa at 400°C are distinctly below the unirradiated value. At 420 to 500 °C, the confidence intervals only allow saying that number densities are similar to the unirradiated value. Similarly, although the average particle number densities are higher in specimens irradiated to 500 dpa than to 100 dpa for all irradiation temperatures, only those at 400 and 420 °C are significantly higher. In particular, for 400 °C the number density of YTiO particles almost doubled from $\sim 1.5 \times 10^{23}$ m$^{-3}$ at 100 dpa to $\sim 3 \times 10^{23}$ m$^{-3}$ at 500 dpa. Overall, the increase in number density as irradiation dose increased from 100 to 500 dpa coincides with further reduction in particle size. The continuing evolution of YTiO particle sizes and number densities past 100 dpa have also been reported by others [18, 28].

Knowing the composition evolution in nanoscale YTiO particles may be an important factor in understanding their stability under irradiation. However, exact quantitative chemical analysis of nanometer-scale oxide particles in APT data is made challenging by field-evaporation chromatic aberrations [64]. This artifact makes the matrix elements appear artificially more concentrated inside nanoscale particles. One way to bypass the issue is to investigate the elemental ratios among Y, Ti, and O, which are considered the main constituents of these oxide particles. The results, in the form of the Y:Ti ratio and the (Y+Ti):O ratio, are shown in Figure 5. Interestingly, in both 100 dpa and 500 dpa experiments, the Y:Ti ratio (upper graph) significantly increased at lower irradiation temperatures, by 50%~100%, and converged to the Y:Ti ratio of unirradiated specimens at higher temperatures. At the same time, (Y+Ti):O ratio (lower graph) is relatively stable across all irradiation temperatures and is approximately the same as the unirradiated material. As will be covered in the discussion section, the increasing Y:Ti ratio may be due to an interplay between ballistic dissolution, displacement energy, and the relative diffusivity of these elements in the matrix.

The ratio between the Y, Ti, and O elements that partitioned in YTiO particles and the Y, Ti, and O elements in the data sets for entire needles are listed in Table 4. This information can be treated as

8

an alternative measure to explore the evolution of YTiO particle chemistry. The data show that all the main constituent elements' fractions inside YTiO particles dropped after ion irradiation, which agrees with the observation that average sizes decrease. The percentages of all three major elements in YTiO particles increased with irradiation temperature, and Y and O fractions gradually converge to unirradiated values. But the Ti fractions remain drastically smaller than the value in unirradiated condition. Further analysis of all data sets revealed that the percentages of Ti were reduced because the amounts of Ti in the APT data sets for entire needles had increased. For example, the average Ti concentration in all APT needles from unirradiated MA957 was 0.54 at%, while it was in the range of 0.6–0.8 at% in ion-irradiated specimens. Thus, the Ti partitioning in YTiO particles appeared to be lessened. We suspect the rise of Ti concentration in entire APT needles derives from the partial dissolution of some large $TiO_2$ particles in materials, although further studies using TEM are needed for confirmation. Another obvious trend from Table 4 is that the percentages of these elements decrease at dose levels above 100 dpa. This behavior is interesting because it suggests that YTiO particle evolution may have not reached a steady state with respect to dose yet. The difference between values at 100 dpa and 500 dpa is most significant in the 400 °C case.

## Alpha Prime (α') Precipitates

Formation of α'/Cr-rich precipitates was observed in specimens irradiated up to 450 °C. Figure 6 shows ion maps of Cr ions, with Cr-rich regions identified by 25% isoconcentration surfaces. High densities of Cr-rich particles were discovered in specimens irradiated by ions at 400 °C and 420 °C. Bands along grain boundaries denuded of Cr-rich particles were seen in ion maps shown in Figure 6(b) and (c). Corresponding snapshots of on-edge grain boundaries and their surroundings are shown in Figure 7, where denuded zones a few nanometers wide can be seen more clearly. Only a few isolated Cr-rich particles were spotted at 450 °C. No Cr-rich regions above the concentration threshold were observed in the analysis volumes for both the unirradiated specimen and the specimen irradiated at 500 °C.

The α' size distributions and a statistical summary are presented in Figure 8 and Figure 9, respectively. The peak of the size distributions shifted to the higher end slightly as irradiation temperature increased from 400 to 420 °C. The sizes may not be statistically accurate for 450 °C due to the limited number of particles. No clear trend was found with respect to different radiation damage levels. But in general, specimens at both 100 dpa and 500 dpa share a similar trend concerning irradiation temperature. The diameters of most α' particles fall in the range of 2.6–3.6 nm. The particle number density rapidly declined from $9.8 \times 10^{23}$ m$^{-3}$ to $0.63 \times 10^{23}$ m$^{-3}$ as irradiation temperature rose from 400 to 450 °C.

9

## Grain Boundary Chemistry

Grain boundary chemistry profiles were generated as described in the experimental section. Segregation of Cr, Ti, TiO, Y, Si, and Ni ions at grain boundaries was observed. In this section, only results for Cr, Ti, TiO, and Y ions are presented in detail because they are more relevant to the study scope. Grain boundary segregation for the other elements of interest is summarized in Table 5. Concentration profiles across grain boundaries and ion maps of the corresponding regions used to generate the profiles are shown in Figure 10–Figure 14 for all available unirradiated and ion-irradiated MA957 APT specimens.

In the unirradiated condition, Cr and Ti were enriched at all three observed grain boundaries, as displayed in Figure 10. Y and TiO ions were occasionally seen located right on a grain boundary— for example, in the data set 06355 (bottom graph) for unirradiated MA957, two of the four YTiO particles happen to be located on the grain boundary. These two YTiO particles caused increased TiO and Y concentration in the corresponding line profiles. Thus, showing TiO ions, rather than O ions alone, helps visualize precipitates near a grain boundary. Note that the Ti signal shown here is for Ti ions only, which does not include Ti from TiO (signal was not decomposed). The TiO-complex ions indicate that the corresponding region is rich in both Ti and O elements. In the unirradiated case, since Y is also correlated with Ti and O, these particles are very likely pre-existing YTiO particles.

Figure 11–Figure 14 present the grain boundary chemistry profiles and the corresponding measurement regions for ion-irradiated MA957 specimens. Depletion of Cr was observed in most data sets from MA957 irradiated below 500 °C, except for a few data sets (06617 in Figure 11 and 05506 in Figure 12), in which Cr exhibited a "W" shaped profile. At 500 °C (Figure 14), one grain boundary (02569) displayed Cr enrichment, while other Cr profiles were "W" shaped. In the cases where Cr depletion was obvious, the lowest concentration usually only went a few percent lower than the matrix Cr concentration. Note that the Cr concentration profiles were calculated excluding α' precipitates when they existed, to avoid further complications in interpreting the 1D profiles.

10

These results suggest that Ti segregation in irradiated MA957 is strongly influenced by temperature. In unirradiated MA957, all three grain boundaries exhibited Ti enrichment to ~2–3 ionic percent. At 400 °C, Ti ions are depleted, from ~0.6–0.8 ionic% in the matrix to a tiny fraction of a percentage at grain boundaries (Figure 11). At the same time, the TiO ion concentration at grain boundaries exhibited a slight increase, though the increase in magnitude is much smaller than the observed Ti ion depletion. With irradiation temperature increase, the Ti segregation transitioned from depletion (Figure 11) to enrichment (Figure 13 and Figure 14). Ti segregation at 420 °C (Figure 12) is more complicated: one grain boundary (05506 in Figure 12) exhibited Ti depletion, while the other three data sets showed no clear segregation. At 450 °C (Figure 13), most of the examined grain boundaries exhibited Ti enrichment, while one (06656-GB1) showed a slight depletion instead. At 500 °C (Figure 14), Ti ions were greatly enriched on two examined grain boundaries. TiO cannot be ignored when considering Ti segregation. Since there is no TiO depletion in any examined grain boundaries, we must check whether the Ti depletion is a result of TiO enrichment. At 400 °C (Figure 11), the concentration of TiO is too low to account for the Ti depletion. In the 05506 and 05507 data sets (Figure 12) and 06655-GB1 (Figure 13), it seems that considering TiO would alter the concentration profile noticeably. However, a closer look reveals that the greatest contribution to the TiO enrichment is from a YTiO particle on the grain boundary, rather than from distributed elements. In other cases where Ti shows enrichment, separating TiO ions only affects the absolute magnitude measurement but cannot affect the observed trend.

The TiO ion segregation behavior is complicated. We are interested in the TiO ion because it often serves as an indicator for YTiO particles when measured together with Y ions, but we found the TiO concentration profile can be different from those of Ti and O ions. In some data sets, such as 05506, 05507-GB2 (Figure 12), 06656-GB2 (Figure 13), and 06695 (Figure 14), we do see strong evidence for the presence of YTiO particles on grain boundaries. Current information is insufficient to determine whether they are pre-existing or newly formed during ion irradiation. On some grain boundaries, an increase of TiO enrichment occurred without having a strong spatial correlation with Y ions, such as grain boundaries in data sets 06693-GB1 and 06654-GB2 in Figure 13, and 06696 in Figure 14. In these data sets, only localized regions of the grain boundary overlap with the Y ion signal, while other TiO-rich regions do not.

11

## Discussion

The APT characterization shows that the YTiO particles in MA957 maintain a high number density ($>1 \times 10^{23}$ m$^{-3}$) and remain nanometer size (2–8 nm in diameter) after ion irradiation to 100 dpa and 500 dpa at 400–500 °C. The result provides experimental evidence of excellent stability of YTiO particles under high-dose irradiation in this temperature range. Since the presence of YTiO particles is crucial for good mechanical strength and creep resistance in ODS alloys, this study suggests that the beneficial effects can survive in long-term radiation exposure.

The stability of YTiO particles is a complex issue, and is typically considered to be affected by multiple mechanisms [65]. For example, from the perspective of the Nelson-Hudson-Mazey (NHM) model, which is based on rate theory, two active competing mechanisms—the ballistic dissolution and the back-diffusion of solute atoms—are responsible for the particle stability [66]. However, the formation and nucleation of new YTiO particles, which is critical to explain the increase in number density, is not considered in that model. YTiO interface coherence may also play a role. Chen et al., explored its effect on stability and suggested that the coherent particles are more stable [25, 67]. Other mechanisms, such as Ostwald ripening, have been proposed to explain the observation of YTiO particle coarsening after ion irradiation [29].

In this study, we have observed a decrease in YTiO particle sizes, with a size distribution that becomes positively skewed at irradiation temperatures of 400 °C and 420 °C in both 100 dpa and 500 dpa specimens. With irradiation temperature increases to 450 °C and 500 °C, the average size and size distribution gradually approach the unirradiated values. This observation fits well into the simple NHM model, where a temperature increase causes an increase in back-diffusion of solute atoms, while ballistic dissolution can be considered thermally insensitive and treated as a constant rate. A similar temperature evolution trend has also been observed in the nanostructured ODS alloy 14YWT [23, 24, 67]. No YTiO particle coarsening was observed in this study. YTiO particle evolution continued up to the maximum applied dose of 500 dpa for all irradiation temperatures, but the changes with dose were greatest at 400 °C and 420 °C. In addition, the compositional analysis in Table 4, where the fractions of ions remaining inside YTiO particles decreased noticeably at 500 dpa compared with 100 dpa and unirradiated specimens, provided further evidence that ballistic dissolution is playing a role. The observation of particle evolution, i.e., size and number density, not reaching a steady state has been reported by Aydogan et al., where 14YWT was irradiated up to ~585 dpa and the microstructure was examined using both TEM and APT [28]. Along with the reduction in size at the lower irradiation temperature, it is tempting to attribute the decrease in number density at 400 °C to ballistic dissolution, however, Certain et al., showed that YTiO particles in 14YWT were only effectively dissolved for irradiation temperatures somewhere below 100°C [23]. Further studies at lower temperatures would be needed to better assess this. The increase of YTiO number density from 100 dpa to 500 dpa at 400 and 420 °C indicating new YTiO particle nucleation and growth under irradiation is a continuous process, and the balance between new particle formation and old particle dissolve had not yet been reached at 100 dpa.

The composition of the YTiO particles measured by APT was nonstoichiometric. Sakasegawa et al. examined unirradiated ODS alloy MA957 using TEM and found that the YTiO particle composition was correlated with particle size [68]. When YTiO particles were smaller than ~18 nm, the Y/Ti ratio was smaller than 1. A similar correlation between the Y/Ti ratio and the particle size has also been reported by Williams et al. [69]. Since most YTiO particles examined in the current study are smaller than 8 nm, the overall measurement of Y/Ti < 1 is consistent with these previous studies. However, in the current study, the Y/Ti ratios inside particles increased by 50%–100% after ion irradiation at 400 °C and 420 °C, compared with unirradiated specimens. At the same time, the YTiO particle sizes slightly decreased. The Y/Ti ratio nevertheless remained smaller than 1, but the shift towards larger ratios during irradiation is thought to be caused by irradiation-induced nonthermal-equilibrium processes. As irradiation temperature increases to 500 °C, thermally driven mechanisms start to play a dominating role in the microstructure evolution, and thus the Y/Ti ratio returns to a level similar to that in the unirradiated material. One possible explanation for the effect of irradiation on Y/Ti ratio is the higher displacement energy of Y than Ti [70], which suggests that Y atoms are less likely to be displaced to the outside of YTiO particles. Although the diffusion of Ti is generally considered much faster than that of Y [71, 72], it may not be sufficient to recover all displaced Ti at lower temperatures. These factors combine to suggest that, at higher temperatures, Ti back-diffusion to YTiO particles will overwhelm the effect of high displacement probability, and the Y/Ti ratio will be driven back to that of the unirradiated material. To fully understand the mechanism behind the imbalance, the Y/Ti ratio under irradiation may require further experiments and detailed atomistic scale modeling.

The formation of α′ precipitates in Fe-Cr systems under thermal aging or irradiation is well known and attributed to the existing miscibility gap [32, 73]. Thermodynamics calculations and experiments show that both spinodal decomposition and nucleation and growth mechanisms are possible for α′ formation in Fe-Cr systems [74, 75]. It is as yet unclear which mechanism is dominant under irradiation, because irradiation could drive materials systems to non-equilibrium states [30, 76] where models that assume equilibrium may not be applicable. Regardless of exact mechanisms, irradiation is found to kinetically accelerate the α-α′ phase separation, likely via radiation enhanced diffusion mechanisms [31, 36, 73, 77]. The acceleration leads to rapid formation of α′ in 9Cr ferritic steels irradiated by neutrons, which have never been observed after thermal aging, although it is thermodynamically indicated. Besides irradiation temperature, irradiation type and dose rate have been found to affect α′ formation as well. In both our own experience and published results from other groups [78-80], self-ion irradiation with dose rates ranging from $10^{-3}$ to $10^{-2}$ dpa/s does not produce α′ precipitates in 9–12Cr ferritic steels within the 300–500 °C temperature range. Reese et al., performed a systematic dose rate dependence study in an ion-irradiated Fe-18Cr alloy and found that the Cr atoms clustering is weaker at the higher the dose rate (measured by the amplitude of the radial distribution function) than lower dose rate [81]. Through qualitative analysis, the authors attributed dose rate dependence to ballistic mixing, where a higher dose rate renders damage cascade more effective as a driving force to remix Cr into Fe.

13

This rationale can be backed up by electron irradiation experiments, where high doses and low ballistic mixing take place, and full-fledged α' precipitates have been observed in a Fe-15Cr alloy at a dose rate comparable to that in the Reese study [82].

In this study, formation of the α' phase was observed for irradiation temperatures up to 450 °C. This observation suggests that the Cr solubility limit in MA957 (14 wt% Cr) is likely between 450–500 °C when subjected to 1.8 MeV Cr ion irradiation with a damage rate of ~$10^{-2}$ dpa/s. The absence of Cr-enriched precipitates at higher temperatures could be attributed to the increased Cr solubility, which makes Cr precipitation unfavorable in these conditions. Similar experimental observations have been reported in other high-Cr alloys under neutron irradiation, and our result agrees with those [30, 83, 84]. The estimated α-α' phase boundary, around 450–500 °C for 14Cr, is consistent with a summarized study by Bonny et al., [30]. Additionally, since there has been no report of observation of α' in both 9Cr and 12Cr ferritic steel under ion irradiation at a similar dose rate in this temperature range, we can safely estimate that the solubility limit within the temperature range, at $10^{-2}$ dpa/s dose rate, is between 12 and 14 wt% Cr.

In 400 °C, 420 °C, and 450 °C specimens, a narrow denuded zone of α' along grain boundaries can be seen in some APT specimens. Based on the discussion in the previous paragraph, the denuded zone can be explained by the depletion of Cr near grain boundaries. This forms a region with effectively lower Cr concentration than the miscibility gap, since 14 wt% Cr already is at the edge of the solubility limit. Note that the size of the denuded zone varies even among specimens with the same irradiation condition. Due to the lack of grain orientation information, we can only suspect that the width is related to misorientation angle and the associated grain boundary sink strength. This observation is consistent with the study by Aydogan et al. on 14YWT using TEM, where denuded zones of α' precipitates with various sizes were observed near grain boundaries [85]. In addition to the co-evolution of grain boundary segregation and α' precipitates, we found, via visual inspection, that α' precipitates mostly formed away from or in-between YTiO particles, rather than on or near the interface (see supplemental video for an example). This anti-correlation between YTiO particles and α' has also been reported in previous literature on neutron irradiation [8, 16]. The underlying mechanism is as yet unclear; one possible hypothesis is that the higher concentration of defects distant from defect sinks at YTiO particle interfaces leads to faster formation of α' precipitates [8, 16].

Radiation-induced segregation of Cr and Ti near grain boundaries was clearly observed. Although there are specimen-to-specimen variations within each irradiation condition, in general, as the irradiation temperature increased from 400 °C to 500 °C, the segregation of Cr on grain boundaries changed from an obvious depletion to a more complicated "W"-shaped profile, while the segregation of Ti ions changed from depletion to enrichment. Ti segregation behavior gradually converged towards the unirradiated condition as temperature increased, but Cr remained relatively

14

depleted even at 500 °C. A higher TiO ion concentration on grain boundaries was observed after ion irradiations at 450 °C and 500 °C, compared to the unirradiated condition. The total Ti content near grain boundaries at these two temperatures was roughly the same as in the unirradiated condition.

Previous studies of RIS in ferritic-martensitic steels [86-88] and ODS ferritic alloys [16, 89, 90] primarily focused on major elements such as Cr, while less attention was paid to elements such as Ti and O. Where comparisons can be made, the tendency for enrichment or depletion of specific elements on the grain boundaries of the unirradiated materials agrees well with other studies. For example, the peak concentration of Ti segregation on grain boundaries in drawn MA957 bars reached ~3 at.% [91], which is almost identical to measured values in this study. In a more recent study, Ti concentration on grain boundaries in Fe-14Cr ODS specimens [92] was found to be similar to the values for the unirradiated MA957 in the current study. Both studies mentioned that the strong segregation behavior of Ti was more prevalent at high-angle grain boundaries. The scatter of the Ti concentrations in the current study is attributed to differences in grain boundary misorientation. Segregation of Ti probably follows an inverse Kirkendall effect [71]. The segregation of O, on the other hand, is less sensitive to irradiation but rather more responsive to temperature effects, since oxygen occupies octahedral sites and travels by interstitial diffusion. The enrichment of both Ti and O could lead to a rise of detected TiO ions on grain boundaries after irradiation at 450 °C and 500 °C. The RIS of Ti and O could lead to impactful effects on oxide particles on the grain boundary. A rational hypothesis based on the RIS behavior can be proposed: the depletion of Ti could cause the dissolution of pre-existing YTiO particles, while enrichment of Ti and O atoms could lead to the formation of additional YTiO particles on boundaries. Because there are few grain boundary areas in current data sets, it is not possible to find direct evidence to prove or disprove this hypothesis. Further studies using in situ ion irradiation or systematic TEM investigation on statistical distribution of oxide particles on grain boundaries will help determine the effects of RIS upon on-boundary YTiO particles.

## Summary

This study presents an extensive microstructural characterization of high-dose ion-irradiated MA957 samples using APT. The result shows that YTiO nano-oxide particles clearly survived up to 500 dpa with only minor changes in particle size, number density, and chemical composition. The observed changes in the YTiO populations is readily rationalized using the NHM model along with assuming that nucleation of new particles is possible. Unlike 9-12 Cr ferritic alloys, the formation of α' was identified in MA957 specimens ion irradiated at temperatures up to 450 °C. The observation of α' at 400-450°C is in good agreement with several reported results for neutron-irradiated ferritic alloys and associated proposed mechanisms. α' denuded zones were observed near grain boundaries and is attributed to a decrease in matrix Cr content near grain boundaries. Cr was enriched on grain boundaries in unirradiated specimens but was predominantly depleted at all temperatures after ion irradiation. Ti underwent a transition from enrichment at 500 °C and 450 °C

to depletion at 420 °C and 400 °C. TiO ions were greatly enriched on grain boundaries at irradiation temperatures between 450 °C and 500 °C.

## Data Availability

The raw/processed data required to reproduce these findings can be shared upon request with approval of the sponsors and PNNL.

RE: Author Statement

> **Comment [AU1]:** CE: Please check the author statement for correctness.

Greetings,

Thank you for the opportunity to revise the paper. We feel that the reviewer input has allowed us to write a better and more thorough paper that addresses all the reviewer comments. The primary focus of our revisions were to A) address the perception by reviewer #1 that the paper lacked scientific content, and B) address concerns by reviewer #2 that the statistical analysis was not sufficient. A brief explanation of our revisions in these areas is provided here.

Scientific Content - In our opinion, the paper never lacked sufficient scientific content, but comparisons of our experimental observations to models/mechanisms were perhaps brief. We have expanded our review of possible mechanisms in the introduction, while in the discussion section, more in-depth comparisons of our results to mechanisms/models are made. However, an in-depth analytic-based mechanism/model analysis was not performed because, in our opinion, the available models/mechanisms can readily describe the observed behaviors.

Statistical Analysis – There often appears to be the presumption by readers that when trends with temperature, dose, etc., fall within the error bands or standard deviations of all the data, the trends are not meaningful. Additional content has been added to justify the trends that we propose. In summary, we better explain and utilize confidence intervals to justify our trends. We also carefully explain in detail why, in practice, it is impossible to obtain tight confidence intervals for number density measurements in microstructure investigations.

16

Numerous other small changes to address other reviewer comments and improve readability have been made.

Best regards,

Jing Wang and Mychailo Toloczko

## Declaration of Competing Interest.

None.

mmc1.zip

## Acknowledgements

## References

[1] G. Was, Z. Jiao, E. Getto, K. Sun, A. Monterrosa, S. Maloy, O. Anderoglu, B. Sencer, M. Hackett, Emulation of reactor irradiation damage using ion beams, Scripta Materialia 88 (2014) 33-36.

[2] G. Odette, M. Alinger, B. Wirth, Recent developments in irradiation-resistant steels, Annu. Rev. Mater. Res. 38 (2008) 471-503.

[3] M.B. Toloczko, D.S. Gelles, F.A. Garner, R.J. Kurtz, K. Abe, Irradiation creep and swelling from 400 to 600 C of the oxide dispersion strengthened ferritic alloy MA957, Journal of nuclear materials 329 (2004) 352-355.

[4] L. Mansur, Theory and experimental background on dimensional changes in irradiated alloys, Journal of Nuclear Materials 216 (1994) 97-123.

[5] M. Swenson, C. Dolph, J. Wharry, The effects of oxide evolution on mechanical properties in proton-and neutron-irradiated Fe-9% Cr ODS steel, Journal of Nuclear Materials 479 (2016) 426-435.

[6] A. Ramar, R. Schäublin, Analysis of hardening limits of oxide dispersion strengthened steel, Journal of Nuclear Materials 432(1) (2013) 323-333.

[7] L. Tan, J. Busby, Formulating the Strength Factor α for Improved Predictability of Radiation Hardening, Journal of Nuclear Materials  (2015).

[8] E. Aydogan, J.S. Weaver, U. Carvajal-Nunez, M.M. Schneider, J.G. Gigax, D.L. Krumwiede, P. Hosemann, T.A. Saleh, N.A. Mara, D.T. Hoelzer, B. Hilton, S.A. Maloy, Response of 14YWT alloys under neutron irradiation: A complementary study on microstructure and mechanical properties, Acta Materialia 167 (2019) 181-196.

[9] S. Yamashita, N. Akasaka, S. Ukai, S. Ohnuki, Microstructural development of a heavily neutron-irradiated ODS ferritic steel (MA957) at elevated temperature, Journal of Nuclear Materials 367 (2007) 202-207.

[10] S. Yamashita, K. Oka, S. Ohnuki, N. Akasaka, S. Ukai, Phase stability of oxide dispersion-strengthened ferritic steels in neutron irradiation, Journal of Nuclear Materials 307–311, Part 1 (2002) 283-288.

[11] S. Yamashita, Y. Yano, S. Ohtsuka, T. Yoshitake, T. Kaito, S.-i. Koyama, K. Tanaka, Irradiation behavior evaluation of oxide dispersion strengthened ferritic steel cladding tubes irradiated in JOYO, Journal of Nuclear Materials 442(1–3) (2013) 417-424.

[12] J. Ribis, S. Lozano-Perez, Nano-cluster stability following neutron irradiation in MA957 oxide dispersion strengthened material, Journal of Nuclear Materials 444(1) (2014) 314-322.

[13] J. Ribis, Structural and chemical matrix evolution following neutron irradiation in a MA957 oxide dispersion strengthened material, Journal of Nuclear Materials 434(1) (2013) 178-188.

[14] I. Monnet, P. Dubuisson, Y. Serruys, M.O. Ruault, O. Kaïtasov, B. Jouffrey, Microstructural investigation of the stability under irradiation of oxide dispersion strengthened ferritic steels, Journal of Nuclear Materials 335(3) (2004) 311-321.

18

[15] M.B. Toloczko, F.A. Garner, S.A. Maloy, Irradiation creep and density changes observed in MA957 pressurized tubes irradiated to doses of 40–110dpa at 400–750° C in FFTF, Journal of nuclear materials 428(1) (2012) 170-175.

[16] N.A. Bailey, E. Stergar, M. Toloczko, P. Hosemann, Atom probe tomography analysis of high dose MA957 at selected irradiation temperatures, Journal of Nuclear Materials 459 (2015) 225-234.

[17] A. London, S. Santra, S. Amirthapandian, B. Panigrahi, R. Sarguna, S. Balaji, R. Vijay, C. Sundar, S. Lozano-Perez, C. Grovenor, Effect of Ti and Cr on dispersion, structure and composition of oxide nano-particles in model ODS alloys, Acta Materialia 97 (2015) 223-233.

[18] T.R. Allen, J. Gan, J.I. Cole, S. Ukai, S. Shutthanandan, S. Thevuthasan, The Stability of 9Cr-ODS Oxide Particles Under Heavy-Ion Irradiation, Nuclear Science and Engineering 151(3) (2005) 305-312.

[19] H. Kishimoto, K. Yutani, R. Kasada, O. Hashitomi, A. Kimura, Heavy-ion irradiation effects on the morphology of complex oxide particles in oxide dispersion strengthened ferritic steels, Journal of Nuclear Materials 367 (2007) 179-184.

[20] M.L. Lescoat, I. Monnet, J. Ribis, P. Dubuisson, Y. de Carlan, J.M. Costantini, J. Malaplate, Amorphization of oxides in ODS materials under low and high energy ion irradiations, Journal of Nuclear Materials 417(1–3) (2011) 266-269.

[21] M. Lescoat, J. Ribis, A. Gentils, O. Kaïtasov, Y. De Carlan, A. Legris, In situ TEM study of the stability of nano-oxides in ODS steels under ion-irradiation, Journal of Nuclear Materials 428(1) (2012) 176-182.

[22] C. Robertson, B. Panigrahi, S. Balaji, S. Kataria, Y. Serruys, M.-H. Mathon, C. Sundar, Particle stability in model ODS steel irradiated up to 100dpa at 600° C: TEM and nano-indentation investigation, Journal of Nuclear Materials 426(1) (2012) 240-246.

[23] A. Certain, S. Kuchibhatla, V. Shutthanandan, D. Hoelzer, T. Allen, Radiation stability of nanoclusters in nano-structured oxide dispersion strengthened (ODS) steels, Journal of Nuclear Materials 434(1) (2013) 311-321.

[24] J. He, F. Wan, K. Sridharan, T.R. Allen, A. Certain, V. Shutthanandan, Y. Wu, Stability of nanoclusters in 14YWT oxide dispersion strengthened steel under heavy ion-irradiation by atom probe tomography, Journal of Nuclear Materials 455(1) (2014) 41-45.

[25] T. Chen, E. Aydogan, J.G. Gigax, D. Chen, J. Wang, X. Wang, S. Ukai, F. Garner, L. Shao, Microstructural changes and void swelling of a 12Cr ODS ferritic-martensitic alloy after high-dpa self-ion irradiation, Journal of Nuclear Materials 467 (2015) 42-49.

[26] M.A. Auger, D.T. Hoelzer, K.G. Field, M.P. Moody, Nanoscale analysis of ion irradiated ODS 14YWT ferritic alloy, Journal of Nuclear Materials 528 (2020) 151852.

[27] S. Santra, S. Amirthapandian, S. Balaji, B.K. Panigrahi, Y. Serruys, C. Robertson, Ion irradiation stability of oxide nano-particles in ODS alloys: TEM studies, Journal of Nuclear Materials 528 (2020) 151861.

[28] E. Aydogan, N. Almirall, G.R. Odette, S.A. Maloy, O. Anderoglu, L. Shao, J.G. Gigax, L. Price, D. Chen, T. Chen, F.A. Garner, Y. Wu, P. Wells, J.J. Lewandowski, D.T. Hoelzer, Stability of nanosized oxides in ferrite under extremely high dose self ion irradiations, Journal of Nuclear Materials 486 (2017) 86-95.

[29] M.L. Lescoat, J. Ribis, Y. Chen, E.A. Marquis, E. Bordas, P. Trocellier, Y. Serruys, A. Gentils, O. Kaïtasov, Y. de Carlan, A. Legris, Radiation-induced Ostwald ripening in oxide dispersion strengthened ferritic steels irradiated at high ion dose, Acta Materialia 78 (2014) 328-340.

[30] G. Bonny, D. Terentyev, L. Malerba, On the $\alpha$–$\alpha'$ miscibility gap of Fe–Cr alloys, Scripta Materialia 59(11) (2008) 1193-1196.

[31] M. Bachhav, G. Robert Odette, E.A. Marquis, $\alpha'$ precipitation in neutron-irradiated Fe–Cr alloys, Scripta Materialia 74 (2014) 48-51.

[32] P.J. Grobner, The 885° f (475° c) embrittlement of ferritic stainless steels, Metallurgical Transactions 4(1) (1973) 251-260.

[33] M.B. Cortie, H. Pollak, Embrittlement and aging at 475 °C in an experimental ferritic stainless steel containing 38 wt.% chromium, Materials Science and Engineering: A 199(2) (1995) 153-163.

[34] J.S. Lee, C.H. Jang, I.S. Kim, A. Kimura, Embrittlement and hardening during thermal aging of high Cr oxide dispersion strengthened alloys, Journal of Nuclear Materials 367-370 (2007) 229-233.

[35] W.-Y. Chen, Y. Miao, Y. Wu, C.A. Tomchik, K. Mo, J. Gan, M.A. Okuniewski, S.A. Maloy, J.F. Stubbins, Atom probe study of irradiation-enhanced $\alpha'$ precipitation in neutron-irradiated Fe–Cr model alloys, Journal of Nuclear Materials 462 (2015) 242-249.

[36] P.D. Edmondson, S.A. Briggs, Y. Yamamoto, R.H. Howard, K. Sridharan, K.A. Terrani, K.G. Field, Irradiation-enhanced α′ precipitation in model FeCrAl alloys, Scripta Materialia 116 (2016) 112-116.

[37] M.J. Alinger, G.R. Odette, G.E. Lucas, Tensile and fracture toughness properties of MA957: implications to the development of nanocomposited ferritic alloys, Journal of Nuclear Materials 307-311 (2002) 484-489.

[38] M.A. Sokolov, D.T. Hoelzer, R.E. Stoller, D.A. McClintock, Fracture toughness and tensile properties of nano-structured ferritic steel 12YWT, Journal of Nuclear Materials 367-370 (2007) 213-216.

[39] H. Hadraba, B. Kazimierzak, L. Stratil, I. Dlouhy, Microstructure and impact properties of ferritic ODS ODM401 (14%Cr-ODS of MA957 type), Journal of Nuclear Materials 417(1) (2011) 241-244.

[40] T.S. Byun, J.H. Yoon, D.T. Hoelzer, Y.B. Lee, S.H. Kang, S.A. Maloy, Process development for 9Cr nanostructured ferritic alloy (NFA) with high fracture toughness, Journal of Nuclear Materials 449(1) (2014) 290-299.

[41] J.H. Kim, T.S. Byun, D.T. Hoelzer, Tensile fracture characteristics of nanostructured ferritic alloy 14YWT, Journal of Nuclear Materials 407(3) (2010) 143-150.

[42] T.S. Byun, J.H. Kim, J.H. Yoon, D.T. Hoelzer, High temperature fracture characteristics of a nanostructured ferritic alloy (NFA), Journal of Nuclear Materials 407(2) (2010) 78-82.

[43] E.A. Marquis, S. Lozano-Perez, V.d. Castro, Effects of heavy-ion irradiation on the grain boundary chemistry of an oxide-dispersion strengthened Fe–12wt.% Cr alloy, Journal of Nuclear Materials 417(1) (2011) 257-261.

[44] J.P. Wharry, G.S. Was, A systematic study of radiation-induced segregation in ferritic–martensitic alloys, Journal of Nuclear Materials 442(1–3) (2013) 7-16.

[45] G.S. Was, J.P. Wharry, B. Frisbie, B.D. Wirth, D. Morgan, J.D. Tucker, T.R. Allen, Assessment of radiation-induced segregation mechanisms in austenitic and ferritic–martensitic alloys, Journal of Nuclear Materials 411(1) (2011) 41-50.

[46] M.L. Hamilton, D.S. Gelles, R.J. Lobsinger, G.D. Johnson, W.F. Brown, M.M. Paxton, A.J. Puigh, C.R. Eiholzer, C. Martinez, M.A. Blotter, Fabrication Technological Development of the Oxide Dispersion Strengthened Alloy MA957 for Fast Reactor Applications, 2000.

[47] M.L. Hamilton, D.S. Gelles, R.J. Lobsinger, M.M. Paxton, W.F. Brown, Fabrication Technology for ODS alloy MA957, 2000.

[48] M.B. Toloczko, F. Garner, V. Voyevodin, V. Bryk, O. Borodin, V. Mel'nychenko, A. Kalchenko, Ion-induced swelling of ODS ferritic alloy MA957 tubing to 500dpa, Journal of Nuclear Materials 453(1) (2014) 323-333.

[49] R.E. Stoller, M.B. Toloczko, G.S. Was, A.G. Certain, S. Dwaraknath, F.A. Garner, On the use of SRIM for computing radiation damage exposure, Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms 310 (2013) 75-80.

[50] J.F. Ziegler, M.D. Ziegler, J.P. Biersack, SRIM–The stopping and range of ions in matter (2010), Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms 268(11) (2010) 1818-1823.

[51] M.P. Short, D.R. Gaston, M. Jin, L. Shao, F.A. Garner, Modeling injected interstitial effects on void swelling in self-ion irradiation experiments, Journal of Nuclear Materials 471 (2016) 200-207.

[52] L. Shao, C.-C. Wei, J. Gigax, A. Aitkaliyeva, D. Chen, B.H. Sencer, F.A. Garner, Effect of defect imbalance on void swelling distributions produced in pure iron irradiated with 3.5 MeV self-ions, Journal of Nuclear Materials 453(1) (2014) 176-181.

[53] J. Wang, M.B. Toloczko, N. Bailey, F.A. Garner, J. Gigax, L. Shao, Modification of SRIM-calculated dose and injected ion profiles due to sputtering, injected ion buildup and void swelling, Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms 387 (2016) 20-28.

[54] P.J. Doyle, K.M. Benensky, S.J. Zinkle, Modeling the impact of radiation-enhanced diffusion on implanted ion profiles, Journal of Nuclear Materials 509 (2018) 168-180.

[55] J. Wang, M.B. Toloczko, K. Kruska, D.K. Schreiber, D.J. Edwards, Z. Zhu, J. Zhang, Carbon Contamination During Ion Irradiation - Accurate Detection and Characterization of its Effect on Microstructure of Ferritic/Martensitic Steels, Scientific Reports 7(1) (2017) 15813.

[56] L. Shao, J. Gigax, H. Kim, F.A. Garner, J. Wang, M.B. Toloczko, Carbon Contamination, Its Consequences and Its Mitigation in Ion-Simulation of Neutron-Induced Swelling of Structural Metals, Proceedings of the 18th International Conference on Environmental Degradation of Materials in Nuclear Power Systems–Water Reactors, Springer, 2018, pp. 681-693.

[57] L. Shao, J. Gigax, D. Chen, H. Kim, F.A. Garner, J. Wang, M.B. Toloczko, Standardization of accelerator irradiation procedures for simulation of neutron induced damage in reactor

structural materials, Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms (2017).

[58] J.G. Gigax, H. Kim, E. Aydogan, L. Price, X. Wang, S. Maloy, F. Garner, L. Shao, Impact of composition modification induced by ion beam Coulomb-drag effects on the nanoindentation hardness of HT9, Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms 444 (2019) 68-73.

[59] K. Thompson, D. Lawrence, D. Larson, J. Olson, T. Kelly, B. Gorman, In situ site-specific specimen preparation for atom probe tomography, Ultramicroscopy 107(2) (2007) 131-139.

[60] O.C. Hellman, J.B. du Rivage, D.N. Seidman, Efficient sampling for three-dimensional atom probe microscopy data, Ultramicroscopy 95 (2003) 199-205.

[61] J. Wang, D.K. Schreiber, N. Bailey, P. Hosemann, M.B. Toloczko, The Application of the OPTICS Algorithm to Cluster Analysis in Atom Probe Tomography Data, Microscopy and Microanalysis 25(2) (2019) 338-348.

[62] L. Yao, M.P. Moody, J.M. Cairney, D. Haley, A.V. Ceguerra, C. Zhu, S.P. Ringer, Crystallographic structural analysis in atom probe microscopy via 3D Hough transformation, Ultramicroscopy 111(6) (2011) 458-463.

[63] M.P. Moody, F. Tang, B. Gault, S.P. Ringer, J.M. Cairney, Atom probe crystallography: Characterization of grain boundary orientation relationships in nanocrystalline aluminium, Ultramicroscopy 111(6) (2011) 493-499.

[64] E.A. Marquis, F. Vurpillot, Chromatic aberrations in the field evaporation behavior of small precipitates, Microscopy and microanalysis 14(06) (2008) 561-570.

[65] J.P. Wharry, M.J. Swenson, K.H. Yano, A review of the irradiation evolution of dispersed oxide nanoparticles in the b.c.c. Fe-Cr system: Current understanding and future directions, Journal of Nuclear Materials 486 (2017) 11-20.

[66] R.S. Nelson, J.A. Hudson, D.J. Mazey, The stability of precipitates in an irradiation environment, Journal of Nuclear Materials 44(3) (1972) 318-330.

[67] T. Chen, J.G. Gigax, L. Price, D. Chen, S. Ukai, E. Aydogan, S. Maloy, F. Garner, L. Shao, Temperature dependent dispersoid stability in ion-irradiated ferritic-martensitic dual-phase oxide-dispersion-strengthened alloy: Coherent interfaces vs. incoherent interfaces, Acta Materialia 116 (2016) 29-42.

[68] H. Sakasegawa, F. Legendre, L. Boulanger, M. Brocq, L. Chaffron, T. Cozzika, J. Malaplate, J. Henry, Y. De Carlan, Stability of non-stoichiometric clusters in the MA957 ODS ferrtic alloy, Journal of Nuclear Materials 417(1) (2011) 229-232.

[69] C.A. Williams, E.A. Marquis, A. Cerezo, G.D. Smith, Nanoscale characterisation of ODS–Eurofer 97 steel: An atom-probe tomography study, Journal of Nuclear Materials 400(1) (2010) 37-45.

[70] I. Monnet, T. Van den Berghe, P. Dubuisson, A comparison between different oxide dispersion strengthened ferritic steel ongoing in situ oxide dissolution in High Voltage Electron Microscope, Journal of Nuclear Materials 424(1–3) (2012) 204-209.

[71] C. Nellis, C. Hin, Radiation induced segregation in quaternary Fe-Ti-Y-O alloys, Journal of Alloys and Compounds 701 (2017) 82-93.

[72] N. Cunningham, Y. Wu, D. Klingensmith, G.R. Odette, On the remarkable thermal stability of nanostructured ferritic alloys, Materials Science and Engineering: A 613 (2014) 296-305.

[73] P. Dubuisson, D. Gilbon, J. Séran, Microstructural evolution of ferritic-martensitic steels irradiated in the fast breeder reactor Phénix, Journal of nuclear materials 205 (1993) 178-189.

[74] T. de Nys, P.M. Gielen, Spinodal decomposition in the Fe–Cr system, Metallurgical Transactions 2(5) (1971) 1423-1428.

[75] T. Barkar, Modelling phase separation in Fe-Cr alloys : A continuum approach, TRITA-ITM-AVL 2018:46, KTH Royal Institute of Technology, Stockholm, 2018, p. 56.

[76] K.C. Russell, Phase stability under irradiation, Progress in Materials Science 28(3) (1984) 229-434.

[77] P. Olsson, J. Wallenius, C. Domain, K. Nordlund, L. Malerba, Two-band modeling of $\ensuremath{\alpha}$-prime phase formation in Fe-Cr, Physical Review B 72(21) (2005) 214119.

[78] J. Wang, m. Toloczko, Accelerator to Accelerator Differences in Radiation Response of HT-9, Pacific Northwest National Laboratory, 2019.

[79] J. Wang, M. Toloczko, High Dose ion Irradiation of a 9Cr Tempered Ferritic/Martensitic Steel, Pacific Northwest National Laboratory, 2019.

[80] C. Pareige, V. Kuksenko, P. Pareige, Behaviour of P, Si, Ni impurities and Cr in self ion irradiated Fe–Cr alloys – Comparison to neutron irradiation, Journal of Nuclear Materials 456 (2015) 471-476.

[81] E.R. Reese, N. Almirall, T. Yamamoto, S. Tumey, G. Robert Odette, E.A. Marquis, Dose rate dependence of Cr precipitation in an ion-irradiated Fe18Cr alloy, Scripta Materialia 146 (2018) 213-217.

[82] O. Tissot, C. Pareige, E. Meslin, B. Decamps, J. Henry, Kinetics of α′ precipitation in an electron-irradiated Fe15Cr alloy, Scripta Materialia 122 (2016) 31-35.

[83] M. Bachhav, G.R. Odette, E.A. Marquis, α′ precipitation in neutron-irradiated Fe–Cr alloys, Scripta Materialia 74 (2014) 48-51.

[84] J. Ribis, S. Lozano-Perez, Orientation relationships and interface structure of α′-Cr nanoclusters embedded in α-Fe matrix after α–α′ demixing in neutron irradiated Oxide Dispersion Strengthened material, Materials Letters 74 (2012) 143-146.

[85] E. Aydogan, E. Martinez, K. March, O. El-Atwani, D.L. Krumwiede, P. Hosemann, T. Saleh, S.A. Maloy, α′ formation kinetics and radiation induced segregation in neutron irradiated 14YWT nanostructured ferritic alloys, Scientific reports 9(1) (2019) 8345-8345.

[86] Z. Lu, R. Faulkner, G. Was, B. Wirth, Irradiation-induced grain boundary chromium microchemistry in high alloy ferritic steels, Scripta Materialia 58(10) (2008) 878-881.

[87] K.G. Field, L.M. Barnard, C.M. Parish, J.T. Busby, D. Morgan, T.R. Allen, Dependence on grain boundary structure of radiation induced segregation in a 9wt.% Cr model ferritic/martensitic steel, Journal of Nuclear Materials 435(1) (2013) 172-180.

[88] J.J. Penisten, The mechanism of radiation-induced segregation in ferritic-martensitic steels, The University of Michigan, 2012.

[89] E.A. Marquis, S. Lozano-Perez, V. De Castro, Effects of heavy-ion irradiation on the grain boundary chemistry of an oxide-dispersion strengthened Fe–12wt.% Cr alloy, Journal of Nuclear Materials 417(1) (2011) 257-261.

[90] J. He, F. Wan, K. Sridharan, T.R. Allen, A. Certain, Y. Wu, Response of 9Cr-ODS steel to proton irradiation at 400° C, Journal of Nuclear Materials 452(1) (2014) 87-94.

[91] M. Miodownik, J. Martin, E. Little, Grain boundary segregation in an oxide-dispersion-strengthened ferritic steel, J Mater Sci Lett 12(11) (1993) 834-835.

[92] J.B. Seol, D. Haley, D.T. Hoelzer, J.H. Kim, Influences of interstitial and extrusion temperature on grain boundary segregation, Y–Ti–O nanofeatures, and mechanical properties of ferritic steels, Acta Materialia 153 (2018) 71-85.

**Figure 1. Comparison of SRIM-calculated and adjusted (a) dose profiles and (b) injected ion profiles, for 1.8 MeV Cr$^{3+}$ at a fluence of $9.1 \times 10^{17}$ ions/cm$^2$ (~500 dpa on average at 100–200 nm depth based on SRIM).**

**Figure 2. Ion maps of Ti, Y, O, TiO, and YO for typical ion-irradiated and unirradiated MA957 APT specimens: (a) 400 °C, 100 dpa; (b) 420 °C, 100 dpa; (c) 450 °C, 100 dpa; (d) 500 °C, 100 dpa; and (e) unirradiated.**

**Figure 3. Size distributions of YTiO particles in unirradiated and ion-irradiated MA957. Results for irradiation to 100 dpa are on the left, and results for irradiation to 500 dpa are on the right.**

**Figure 4. Statistical values of diameter and number density of YTiO particles for unirradiated (solid gray line) and ion-irradiated MA957.**

**Figure 5. Comparison of elemental ratios in YTiO particles in unirradiated (the solid gray line) and ion-irradiated MA957 specimens.**

**Figure 6. Ion maps of Cr for unirradiated and ion-irradiated MA957: (a) unirradiated; (b) 400 °C, 100 dpa; (c) 420 °C, 100 dpa; (d) 450 °C, 100 dpa; (e) 500 °C, 100 dpa. The isoconcentration surfaces were constructed using Cr ions at 25% to highlight Cr-rich precipitates.**

**Figure 7. Magnified view near grain boundaries (almost on-edge) showing zones denuded of α′. The cyan point clouds are Ti ions, showing the locations of grain boundaries, and the magenta isosurfaces show the α′ using 25% Cr ion concentration.**

Figure 8. Size distributions of α' in MA957 irradiated with ions at different temperatures and damage levels.

**Figure 9. Comparison of average α' diameter and number density among MA957 samples irradiated by ions. The gray dashed lines were drawn by hand, only to guide the visualization of data trends.**

**Figure 10. Cr, Ti, TiO, and Y concentration profiles across grain boundaries in unirradiated MA957. Corresponding ion maps of regions of interest are shown on the right side. The data set IDs are enclosed in parentheses.**

**Figure 11. Cr, Ti, TiO, and Y concentrations measured near grain boundaries in MA957 ion-irradiated to 100 dpa at 400 °C. Ion maps of regions used to generate concentration profiles are shown on the right side. The data set IDs are shown in parentheses. To avoid interference of α'/Cr-rich precipitates, particles identified as such were removed before 1D profile generation.**

**Figure 12. Cr, Ti, TiO, and Y concentrations measured near grain boundaries in MA957 ion-irradiated to 100 dpa at 420 °C. Corresponding ion maps of regions of interest are shown on the right side. The data set IDs are shown in parentheses. To avoid interference of α'/Cr-rich precipitates, particles identified as such were removed before the 1D profile generation.**

**Figure 13. Cr, Ti, TiO, and Y concentrations measured near grain boundaries in MA957 ion-irradiated to 100 dpa at 450 °C. Corresponding ion maps of regions of interest are shown on the right side. The data set IDs are listed in parentheses. To avoid interference of α'/Cr-rich precipitates, particles identified as such were removed before 1D profile generation.**

**Figure 14. Cr, Ti, TiO, and Y concentrations measured near grain boundaries in MA957 ion-irradiated to 100 dpa at 500 °C. Corresponding ion maps of regions of interest are shown on the right side. The data set IDs are listed in parentheses.**

Table 1. Nominal composition (wt%) of the examined material.

| Alloy | Tube ID | Heat | Fe | Cr | Ni | Mn | Mo | Si | C | V | Ti | $Y_2O_3$ |
|-------|---------|------|-----|-----|------|------|------|------|-------|---|------|----------|
| MA957 | EV | DBB0111 | Bal. | 13.8 | 0.13 | 0.05 | 0.31 | 0.05 | 0.014 | — | 1.05 | 0.22 |

Table 2. Summary of study characteristics for all MA957 APT specimens examined.

| Temp (°C) | DPA (dpa) | No. of APT Tips | Total Ions (million) | Volume ($\times10^6$ nm$^3$) |
|-----------|-----------|-----------------|----------------------|------------------------------|
| NA | Unirrad. | 8 | 49 | 1.56 |
| 400 | 100 | 9 | 143 | 4.57 |
|     | 500 | 5 | 39 | 0.93 |
| 420 | 100 | 6 | 65 | 2.07 |
|     | 500 | 7 | 58 | 1.84 |
| 450 | 100 | 6 | 47 | 1.65 |
|     | 500 | 3 | 22 | 0.70 |
| 500 | 100 | 8 | 75 | 2.39 |
|     | 500 | 4 | 10 | 0.33 |

Table 3. Mean, standard deviation (σ), number of measurements (Data #), and margin of error (MOE) for 95% confidence interval of mean for size and number density of YTiO particles.

| Dose (dpa) | Temp (°C) | Diameter (nm) | | | | Number Density ($\times10^{23}$/m$^3$) | | | |
|------------|-----------|------|---|--------|------|------|---|--------|------|
|            |           | Mean | σ | Data # | MOE* | Mean | σ | Data # | MOE* |
| Unirradiated | | 4.36 | 1.66 | 360 | 0.17 | 3.00 | 1.22 | 8 | 1.02 |
| 100 | 400 | 3.40 | 1.59 | 587 | 0.13 | 1.50 | 0.87 | 9 | 0.67 |
|     | 420 | 3.90 | 1.63 | 378 | 0.16 | 2.59 | 1.22 | 6 | 1.28 |
|     | 450 | 3.88 | 1.70 | 449 | 0.16 | 2.98 | 1.33 | 6 | 1.40 |
|     | 500 | 4.15 | 1.61 | 450 | 0.15 | 2.35 | 1.36 | 8 | 1.14 |
| 500 | 400 | 2.92 | 1.32 | 457 | 0.12 | 3.02 | 1.11 | 5 | 1.37 |

27

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| 420 | 3.21 | 1.39 | 550 | 0.12 | 3.88 | 1.51 | 7 | 1.40 |
| 450 | 3.76 | 1.49 | 218 | 0.20 | 3.65 | 1.38 | 3 | 3.43 |
| 500 | 3.78 | 1.30 | 70 | 0.30 | 2.94 | 0.53 | 4 | 0.88 |

*Note: the MOE, margin of error, for diameter was calculated based on number of particles, while for number density it was calculated based on number of examined APT specimens.

Table 4. Percentage of Y, Ti, and O in YTiO particles relative to the entire sample (i.e., the ratio between counts of Y inside clusters versus counts of Y in the entire APT needle) in ion-irradiated MA957.

| Irrad. Temp. (°C) | Y in clusters/Y in APT needle (%) | | | Ti in clusters/ Ti in APT needle (%) | | | O in clusters/O in APT needle (%) | | |
|---|---|---|---|---|---|---|---|---|---|
| | Unirrad. | 100 dpa | 500 dpa | Unirrad. | 100 dpa | 500 dpa | Unirrad. | 100 dpa | 500 dpa |
| 400 | 63.9 ± 11.0 | 47.5 ± 10.9 | 21.4 ± 3.6 | 28.7 ±12.6 | 5.8 ± 2.0 | 3.1 ± 0.9 | 40.3 ± 10.5 | 28.5 ± 11.6 | 8.5 ± 3.0 |
| 420 | | 53.5 ± 10.7 | 47.6 ± 13.7 | | 12.1 ± 4.1 | 9.2 ± 3.2 | | 35.1 ± 9.3 | 28.8 ± 11.7 |
| 450 | | 54.1 ± 6.0 | 53.0 ± 2.3 | | 13.8 ± 3.7 | 11.1 ± 3.3 | | 31.8 ± 6.5 | 27.7 ± 8.6 |
| 500 | | 57.6 ± 8.4 | 47.0 ± 7.7 | | 13.5 ± 5.7 | 13.9 ± 5.2 | | 36.1 ± 9.7 | 21.3 ± 8.2 |

Table 5. Summary of radiation-induced segregation at grain boundaries for several elements of interest. "+," "0," and "–" mean enrichment, no change/not sure, and depletion, respectively. Since multiple APT needles were examined for each condition, different behaviors can be seen across specimens. In this case, "," means "and" to list all observed segregation types.

| Dose (dpa) | Temperature (°C) | No. of Grain Boundaries Examined | Cr | Ni | Si | Y | Ti | TiO | O |
|---|---|---|---|---|---|---|---|---|---|
| Unirrad. | — | 3 | + | 0,+ | + | 0,+ | + | 0,+ | 0,+ |
| 100 | 400 | 4 | – | + | + | 0,+ | – | 0,+ | 0,+ |
| | 420 | 4 | – | + | + | 0,+ | –,+ | 0,+ | 0,+ |
| | 450 | 7 | – | + | + | 0,+ | –,+ | + | 0,+ |
| | 500 | 3 | –,+ | + | + | 0,+ | + | + | + |

28

29