The comparison of microstructure and nanocluster evolution in proton and neutron irradiated Fe-9%Cr ODS steel to 3 dpa at 500°C

M.J. Swenson^{1*}, and J.P. Wharry¹

¹Boise State University, 1910 University Drive, Boise, ID 83725, USA

*Corresponding Author

Name: Matthew J. Swenson

Postal Address: 1910 University Drive, Boise, ID 83725, USA

Telephone Number: +1 503 830 4231

E-mail address: matthewswenson1@u.boisestate.edu

The comparison of microstructure and nanocluster evolution for proton and neutron irradiated Fe-9%Cr ODS steel to 3 dpa at 500°C

M.J. Swenson^{1*}, and J.P. Wharry¹

¹Boise State University, 1910 University Drive, Boise, ID 83725, USA

Abstract

A model Fe-9%Cr oxide dispersion strengthened (ODS) steel was irradiated with protons or neutrons to a dose of 3 displacements per atom (dpa) at a temperature of 500°C, enabling a direct comparison of ion to neutron irradiation effects at otherwise fixed irradiation conditions. The irradiated microstructures were characterized using transmission electron microscopy and atom probe tomography including cluster analysis. Both proton and neutron irradiations produced a comparable void and dislocation loop microstructure. However, the irradiation response of the Ti-Y-O oxide nanoclusters varied. Oxides remained stable under proton irradiation, but exhibited dissolution and an increase in Y:Ti composition ratio under neutron irradiation. Both proton and neutron irradiation also induced varying extents of Si, Ni, and Mn clustering at existing oxide nanoclusters. Protons are able to reproduce the void and loop microstructure of neutron irradiation carried out to the same dose and temperature. However, since nanocluster evolution is controlled by both diffusion and ballistic impacts, protons are rendered unable to reproduce the nanocluster evolution of neutron irradiation at the same dose and temperature.

Keywords: transmission electron microscopy (TEM), atom probe tomography (APT), oxide dispersion strengthened steel

1 Introduction

The growing global demand for energy will increasingly call upon fusion and advanced nuclear fission reactors to supply safe and reliable energy worldwide. These reactor designs require structural and cladding materials that can withstand temperatures up to 700°C, and irradiation doses up to several hundred displacements per atom (dpa) [1–3]. Oxide dispersion strengthened (ODS) steels are candidates for advanced reactor cladding materials and fusion first wall and blanket structures, due to their high-temperature strength and dimensional stability under irradiation [4–13]. Proton irradiations are increasingly being used to evaluate the integrity of these materials by simulating the neutron service environment at an accelerated rate. The use of proton irradiations to emulate the neutron irradiated microstructure has been validated for fcc Fe-Ni-Cr alloys [14], but has not yet been validated for bcc Fe-Cr alloys nor for ODS alloys.

A critical component of the microstructure of ODS steels is their high density of Ti-Y-O-rich nanoclusters, which strengthen the material without significantly compromising ductility. These nanoclusters also act as localized sinks for point defects, providing resistance to irradiation swelling [4–6,8–10,12]. It is desirable to evaluate the stability of these nanoclusters under irradiation.

Atom probe tomography (APT) is an established technique for analyzing nanoclusters such as the Ti-Y-O oxides. An objective three-dimensional atomic model is reconstructed, and nanocluster analysis is carried out using the maximum separation envelope [15] method within each sample reconstruction. However, cluster analysis is highly sensitive to the definition of specific analysis parameters such as $d_{\max}$ and $N_{\min}$ for the execution of the analysis, and the

measured results of the cluster analysis can often be highly sensitive to these parameters , which define the maximum separation distance and the minimum number of adjacent atoms required for the software to identify a cluster, respectively [15–19]. Several authors [15–19] have proposed varying strategies for the identification and application of these parameters to improve the accuracy of the APT cluster analysis. APT is used to complement transmission electron microscopy (TEM) to provide atomic-level resolution of clusters that are smaller than the resolution of conventional TEM.

The objective of this study is to determine whether proton and neutron irradiation, at a fixed dose and temperature, produce equivalent microstructures in an Fe-9%Cr model ODS alloy. A comparison will be drawn between the evolution of microstructural response to proton and neutron irradiation at a common dose and temperature. Particular emphasis will be placed on the APT results and the chemical evolution of the Ti-Y-O oxide nanoclusters within the matrix. The APT cluster analysis and considerations for optimization of the cluster measurement parameters will be presented. Finally, an evaluation of proton irradiation as a surrogate for neutron irradiation at these conditions will be discussed.

2 Experiments

2.1 Material and irradiations

A rod of Fe-9%Cr ODS martensitic steel material (composition provided in [Table 1](#)) was provided by the Japan Nuclear Cycle Development Institute (now known as the Japan Atomic Energy Agency). Alloyed ferritic steel was mechanically mixed with Y_2O_3 powders that were hot

extruded at 1150°C. Finally, the rod was heat treated at 1050°C for 1 hour, air cooled, then tempered at 800°C with subsequent air cooling. Additional details regarding the mechanical alloying and fabrication of the sample rod may be found in [20]. Two sets of specimens were fabricated from the rod: one set for proton irradiations, and another set for neutron irradiations. Both the proton and neutron irradiations were carried out to 3 dpa at 500°C, to enable a comparison of irradiation effects across different dose rates and irradiating particles, but at otherwise consistent conditions.

Proton irradiation specimens were cut by electrical discharge machining into 1.5 mm x 1.5 mm x 20 mm bars. The bars were mechanically polished through 4000 grit SiC paper, followed by electropolishing to remove the plastic deformation introduced by mechanical polishing. Specimens were electropolished for 20 seconds in a 10% perchloric acid + 90% methanol solution maintained at -40°C, with a 35 V applied potential between the specimen (anode) and platinum mesh cathode. These specimens were then irradiated with 2.0 MeV protons in a 1.7 MV General Ionex Tandatron accelerator at the Michigan Ion Beam Laboratory. The accelerator beam line was maintained at pressures below 1.3×10^{-5} Pa (10^{-7} torr) throughout the experiment. Specimens were mounted onto a copper irradiation stage, which was electrically isolated from the accelerator beam line, to allow for accurate charge collection. Thermocouples were spot-welded onto the specimen and were used to calibrate a 2D infrared thermal pyrometer. The pyrometer recorded the temperatures of three areas of interest on the specimen at 0.1 Hz throughout the experiment. A shim filled with liquid indium sandwiched between the specimens and stage provided efficient heat application or removal from the specimens; a combination of resistance heating and air cooling were used to maintain the irradiation temperature at $500 \pm 10^\circ\text{C}$.

Prior to proton irradiation, the size of the focused proton beam was measured in a beam profile monitor and was found to have a FWHM of no more than 3 mm. During irradiation, the focused proton beam was raster-scanned across samples at a frequency of 2061 Hz in the vertical direction and 255 Hz in the horizontal direction. The duration of one scanning cycle in the vertical direction is 0.48 ms, and 3.9 ms in the horizontal direction. The ratio of these two scanning cycles is a non-integer number, which ensures that the beam path is offset from the previous scan cycle, which provides good spatial uniformity of the scanned beam area. [Figure 1a](#) illustrates this scanning pattern overlaid onto apertures which define the irradiation area on the samples. The resulting beam current density was $\sim 22 \mu\text{A}/\text{cm}^2$, yielding a dose rate of $\sim 1 \times 10^{-5}$ dpa/sec.

At the time of irradiation, the displacement damage of 3 dpa and the damage depth profile were calculated with the Stopping and Range of Ions in Matter (SRIM-2008) program [21] in “Detailed Calculation” mode and the displacements were obtained from the vacancy.txt file. A flux of 2.0 MeV protons normal to Fe-9%Cr produces a relatively uniform damage profile between 1 μm and 10 μm , with a damage peak at approximately 19 μm (shown in [Figure 1b](#)). All microstructural analyses of proton-irradiated specimens were conducted at depths of 1–7 μm , in order to avoid surface effects and the steep irradiation dose gradient at the damage peak. [Subsequently, Stoller, et al. have shown that SRIM calculations are more accurate when conducted in “Quick Calculation” (K-P) mode and the energy partition results are used to obtain the estimate for displacements per ion [22]. With this recommended calculation method, and at these analysis depths, the accumulated dose would be ~ 1.6 – 2.1 dpa.]

Neutron irradiation specimens were cut into transmission electron microscopic (TEM) discs, 3 mm in diameter, and approximately 150-200 μm thick. Discs were also mechanically

polished through 4000 grit SiC paper, followed by electropolishing at -30°C in 10% perchloric acid + 90% methanol. The discs were irradiated in a fast neutron spectrum (dose rate $\sim 10^{-7}$ dpa/sec) in the Advanced Test Reactor (ATR) at the Idaho National Laboratory to a dose of 3 dpa. Irradiation began in September 2008 as part of the pilot project for the ATR National Scientific User Facility. The irradiation temperature of 500°C was determined with SiC electrical resistivity samples placed in experiment capsules; thermal models, in which the gas-gap distance was adjusted, correlated the SiC experimental data [23].

2.2 Transmission electron microscopy

TEM analysis was conducted to evaluate microstructure evolution under proton or neutron irradiation. TEM lamellae were prepared for the as-received and irradiated conditions using the same focused ion beam (FIB) lift-out technique on an FEI Quanta 3D FEG FIB at the Center for Advanced Energy Studies (CAES). TEM lamellae were cut and lifted perpendicular to the surface of the bulk. In the case of proton irradiation, this orientation provided a cross-section of the damage profile through the depth of the TEM film. Prior to milling, all specimen surfaces were protected with a 3 μm platinum deposit, which ensured that the original proton-irradiated surface was retained for reference. Each sample was milled at 30 kV to an estimated thickness of ~ 100 nm, width of ~ 15 μm , and depth of ~ 7 μm (Figure 2a). The samples were subsequently milled at 5 kV to an estimated thickness of 50-100 nm, followed by cleaning at 2 kV for approximately 1 minute on each side. The purpose of the cleaning process was to reduce any surface damage to the sample caused by the milling.

Microstructure analysis focused on characterizing the size and number density of grains, dislocations, carbide precipitates, voids, and dislocation loops. TEM specimens were analyzed using an FEI Tecnai TF30-FEG scanning transmission electron microscope (STEM) at CAES. Grains and carbides were imaged in bright field mode throughout the analysis region available in the sample film. Voids were imaged in bright field mode using the through-focus technique. Dislocation line density was determined by measuring the linear density of dislocations in perpendicular directions and calculating an effective area density. Dislocation loops were imaged in STEM mode following a procedure outlined by Parish et al. [24] in which small collection (β) and convergence (α) angles are applied to create a STEM bright field image. For loops that were imaged close to an “edge-on” condition, the longer dimension observed was taken to be the loop diameter [25]. Oxide clusters were imaged in bright field mode in areas with low dislocation contrast so that any z-contrast of the oxides would be more apparent. Finally, the specimen thickness was measured with electron energy loss spectroscopy (EELS). Image collection and analysis was conducted using Digital Micrograph software.

2.3 Atom probe tomography

Atom probe tomography (APT) complimented the TEM analysis by enabling atomic-resolution characterization. Resolution limitations of the TEM precluded a thorough analysis of the oxide nanoclusters and nanoscale phases; this data was obtained via APT. APT needles were fabricated using an FEI Quanta 3D FEG FIB for the as-received, proton-irradiated, and neutron-irradiated specimens at CAES. Sample wedges $\sim 2\ \mu\text{m}$ wide and $\sim 3\ \mu\text{m}$ deep were cut and lifted in a direction perpendicular to the surface of the material for the as-received and neutron-irradiated specimens. The wedges were subsequently mounted onto silicon posts and partitioned, resulting in 6-8 APT tips each. The tips were then milled using annular ring patterns to shape them into needles with a tip radius $\leq 50\ \text{nm}$ [26], as shown in [Figure 2b](#). The needle was sharpened such that the tip of the needle was positioned just below the irradiated bulk surface. Larger wedges were milled from the proton-irradiated specimen, such that the needle tip would be situated $\sim 1\ \mu\text{m}$ below the irradiated surface.

Each needle was analyzed with a Cameca LEAP 4000X HR at CAES, operated in laser pulsed mode with samples held at 40 K. Laser power ranged from 40-70 pJ, with a pulse repetition rate of 200 kHz. Each data set was reconstructed with the Integrated Visualization and Analysis Software (IVAS) Version 3.6.2 using an SEM image of the needle profile and a tip radius between 3-10 nm. Each tip rendering was visually inspected to ensure the tip volume was consistent with the SEM image prior to the analysis, and that the existing cluster morphology was consistent with that observed via TEM.

Elements are identified using their mass-to-charge ratio, with peaks based on overall isotope abundance given the known composition of the material. Some peaks overlap, such as those of $^{58}\text{Fe}^{2+}$ and $^{58}\text{Ni}^{2+}$ at a mass-to-charge ratio of 29. This peak was identified to be $^{58}\text{Fe}^{2+}$

because the bulk concentration of Fe is ~1500 times that of Ni, although it is probable that a minority of these ions are $^{58}\text{Ni}^{2+}$. With smaller data sets, specifically those containing fewer than 2 million ion counts, it is not possible to distinguish all of the elemental mass-to-charge ratio peaks. Data sets used in the present analysis ranged in size from 2.7 million to 31 million ion counts per needle.

Cluster analysis was performed on each tip (excluding those volumes attributed to carbides or grain boundaries) using the maximum separation method [15] with the cluster analysis module within the IVAS software. Accuracy of the cluster analysis relies primarily upon two parameters: d_{max} , the maximum separation distance between atoms in a cluster, and N_{min} , the minimum number of atoms to be considered a cluster. Both d_{max} and N_{min} are determined independently for each specimen condition (as-received, proton-irradiated, and neutron-irradiated). Appropriate d_{max} and N_{min} values depend upon the amount of solute concentration and the relative distribution of the solutes within the matrix [18,19]. Since other authors have observed composition changes of nanoclusters under irradiation [8,9,13,27–30], it was expected that the d_{max} and N_{min} values could differ for each condition. Appropriate d_{max} and N_{min} values were selected for each condition following the approach proposed by Kolli and Seidman [16] and further refined by Williams, et al. [19], in which the selected d_{max} yielded a minimum number of counted clusters by the analysis. [Figure 3](#) shows typical plots of d_{max} vs. cluster count for each condition studied. In all cases, when d_{max} values were too small, a “cluster of clusters” effect was present in which the software identified a single cluster as a group of smaller clusters clumped together. This effect overinflated the number density of clusters, while under-estimating their average size. Conversely, when d_{max} values were too large, additional clusters were spuriously generated and counted, which also overinflated the number density.

Values for $N_{\min}$ were selected in order to minimize the amount of random clusters identified.

Table 2 summarizes the cluster analysis parameters selected for each condition. Parameter selection was conducted for each tip, but it was found that the appropriate $d_{\max}$ and $N_{\min}$ values were consistent across all tips from a given condition. Once the parameters were selected, a visual inspection of each cluster rendering confirmed the identified clusters were consistent with those that could be seen in the original APT reconstruction.

The IVAS cluster analysis output file provides values for R_{gx} , R_{gy} and R_{gz} for each cluster, which is taken to be the respective radius of gyration in each coordinate direction. An overall radius of gyration (R_g) for each cluster was calculated by [31]:

$$R_g = \sqrt{R_{gx}^2 + R_{gy}^2 + R_{gz}^2} \quad (1)$$

and the Guinier diameter (D_G) for each cluster was determined using [31,32]:

$$D_G = 2\sqrt{\frac{5}{3}} R_g \quad (2)$$

The average and standard deviation was calculated across all clusters measured and the error propagation formula was used to calculate an overall standard deviation for the Guinier diameter.

The standard deviation of the mean was also calculated to evaluate the relative certainty of the mean diameter. The cluster number density (N_{nc}) was determined by:

$$N_{nc} = \frac{\sum N_c}{\sum V_T} \quad (3)$$

where $\sum N_c$ is the total number of clusters identified in all tips from a given condition and $\sum V_T$ is the total analyzed volume in all tips from that condition. The volume fraction of clusters (f_v) was calculated using:

$$f_v = \frac{\sum N_{cl}}{N_{tot}} \quad (4)$$

where $\sum N_{cl}$ is the total number of atoms within the measured clusters and N_{tot} is the total number of atoms within the combined reconstructed volumes from all sample tips [33].

Additional IVAS cluster analysis output data includes the elemental composition of each cluster identified, along with the composition of the matrix surrounding the clusters. Using this data, the average composition in at% was calculated for each cluster. Note that the measured amounts of Fe and Cr may be overinflated within the clusters due to trajectory aberrations [19,34]. Additional calculations enabled by the cluster analysis output data were conducted. The percentage of each element contained within clusters (f_{cl}^i) was found using:

$$f_{cl}^i = \frac{\sum N_{cl}^i}{N_{tot}^i} \quad (5)$$

where $\sum N_{cl}^i$ is the number of total number of species atoms within the clusters and N_{tot}^i is the total number of species atoms within the combined reconstruction volumes. Finally, the ratio of Y:Ti atoms and the (Y+Ti):O ratio were calculated for each cluster and averaged. These additional calculations provide insight into the irradiation evolution of the composition of the oxide nanoclusters [9,13] and other irradiation-induced phases.

3 Results

3.1 Transmission electron microscopy

TEM imaging was used to observe the microstructure of irradiated and as-received specimens. Grains, dislocation lines, and carbides exhibited stability under proton and neutron irradiations, while dislocation loops and voids were nucleated. Bright field images of the general structure and dislocation network for each condition are shown in [Figure 4](#), while quantitative TEM microstructure results are provided in [Table 3](#) for all specimen conditions.

Approximately 100 grains and the carbide precipitates contained within them were measured from each condition. Grains and carbides exhibited little change with irradiation, having diameters ranging 0.23–0.31 μm and 0.07–0.11 μm , respectively. All diameter variations fell within the standard deviation of the measurements. Similarly, the dislocation line density varied over $17.6\text{--}19.1 \times 10^{14} \text{ m}^{-2}$ with a standard deviation up to $5.3 \times 10^{14} \text{ m}^{-2}$; Based on these relatively narrow bands of size and density measurements, and their corresponding wide standard deviations, there is no evidence to suggest that these features have dramatically evolved in response to either irradiation condition.

Small irradiation-induced voids, 3–7 nm in diameter, were observed at a low number density of $0.24\text{--}0.34 \times 10^{21} \text{ m}^{-3}$ in both the proton- and neutron-irradiated specimens. TEM micrographs of typical voids are shown in [Figure 5](#) for the proton- and neutron-irradiated conditions, respectively. Within these images, it was found that a high density of Fresnel contrast was present in all conditions using the through-focus technique. The majority of this contrast was attributed to the high density of oxide nanoclusters and not as voids. The oxide contrast typically exhibited contrast without a hollow center in the over- or under-focused conditions and the larger oxides were usually still visible in the in-focused condition. On the other hand, a small fraction of these features exhibited more distinct contrast with a solid bright center in the under-focused condition and a solid dark center in the over-focused condition, while not being visible when the

sample was in-focus (Figure 6). These latter features were identified to likely be voids. Overall, these voids were relatively scarce and sparsely distributed through the specimens.

Dislocation loops were imaged in STEM mode at the [001] and [111] zone axes. A total of 688 loops were measured in the proton-irradiated sample, and 182 loops were measured in the neutron-irradiated sample. For each zone axis imaged, dislocation loop orientation maps generated by Yao, et al. [25] were used to determine that the loops commonly resided on the {111} or {001} habit planes [25]. Dislocation loops produced by proton and neutron irradiation are similar in size, at 8.4 ± 1.7 and 8.9 ± 2.0 nm, respectively, and similar in number density, at $(10.2 \pm 8.0) \times 10^{21} \text{ m}^{-3}$ and $(2.3 \pm 1.2) \times 10^{21} \text{ m}^{-3}$, respectively. STEM micrographs of typical distributions of dislocation loops are shown in Figure 6, along with a histogram showing a comparable size distribution from both proton and neutron irradiations. By considering the dislocation loop diameter as a multinomial distribution the errors were calculated as

$$[35]: \text{Var}(\% \text{ of Total}) = p_i(1 - p_i) \quad (6)$$

where p_i is the % of Total for each size range.

Bright field images of the oxide clusters were obtained by reviewing areas that had low dislocation contrast, which allowed the z-contrast of the clusters to be more visibly prominent. For the as-received specimen, the clusters appeared to be homogeneously distributed (Figure 7a). A similar distribution was observed with the proton-irradiated specimen (Figure 7b). On the other hand, with the neutron-irradiated specimen, the z-contrast of the clusters did not appear to be as prominent in the images (Figure 7c). Note that the local thickness of each sample for these images varies between 50 to 100 nm, so the perceived density of the clusters in each image cannot be directly compared. In addition, it becomes difficult to resolve any nanoclusters that

are less than 2 nm in diameter [6,24]. As a result, atom probe tomography was also conducted to achieve a more objective determination of the oxide nanocluster average size and number density.

3.2 Atom probe tomography

The atomic-level resolution of APT with IVAS cluster analysis enabled the characterization of the irradiation-induced dissolution of oxide nanoclusters, and the irradiation-induced formation of Si-, Ni-, and Mn-rich clusters. The 3D reconstructions of the as-received specimens exhibit clustering of Ti, O and Y atoms along with TiO, YO, FeO, and CrO compounds all at coincident locations in the matrix. For this reason, all of these atoms/compounds were chosen for the oxide cluster analysis. The same atoms/compounds are clustered in both the proton- and neutron-irradiated specimens as well, but there is also evidence of clustering among the Si, Mn, and Ni atoms at the same locations. A total of 3 different LEAP tips were analyzed from each of the as-received and neutron- irradiated specimens, while 7 were analyzed from the proton-irradiated specimen. Representative atom distribution maps, as created by LEAP analysis and 3D reconstruction, are shown in [Figures 8-10](#) for the as-received, proton-irradiated, and neutron-irradiated conditions, respectively.

Cluster analysis using IVAS software enabled quantification of the oxide nanocluster sizes and number densities ([Table 4a](#)). A total of 486, 964, and 355 oxide nanoclusters were identified and analyzed in the as-received, proton-irradiated, and neutron-irradiated specimens, respectively. Proton irradiation caused the average size of the nanoclusters to decrease from 5.96

± 3.10 nm to 4.77 ± 1.91 nm, at a similar number density ($568 \times 10^{21} \text{ m}^{-3}$ as-received, to $560 \times 10^{21} \text{ m}^{-3}$ proton-irradiated). However, neutron irradiation induced a more significant decrease in nanocluster size and number density, to 3.41 ± 1.69 nm at $435 \times 10^{21} \text{ m}^{-3}$. Both the decline in average size and number density of the nanoclusters are reflected in the reduced volume fraction and suggest partial dissolution of the nanoclusters into the matrix. A comparison of the overall size distribution of nanoclusters in each condition is illustrated in [Figure 11](#).

Chemical analysis of the clusters also suggested greater cluster stability under proton irradiation than under neutron irradiation. In reviewing the % of each atomic specie in clusters (f_{cl}^i), it is helpful to compare this value to the overall volume fraction (f_v) in clusters. The difference between these values provides a sense of the relative extent to which each specie clusters. The amount of clustering of Y, Ti, and O after proton irradiation is relatively stable. Meanwhile, there is a notable decrease in f_{cl}^Y , f_{cl}^{Ti} , and f_{cl}^O ([Table 4a](#)) and the relative amount of clustering $f_{cl}^Y - f_v$, $f_{cl}^{Ti} - f_v$, and $f_{cl}^O - f_v$ ([Figure 12](#)), following neutron irradiation. The most de-clustering is measured for Ti; prior to irradiation, 71% of all Ti ions collected were located in clusters, compared to only 24% clustered following neutron irradiation. In addition, the % clustered of Si, Mn, and Ni (f_{cl}^{Si} , f_{cl}^{Mn} , and f_{cl}^{Ni}) increase with irradiation ([Table 4a](#) and [Figure 12](#)). This is consistent with review of the 3D atom distribution maps ([Figures 9](#) and [10](#)) which show visual evidence of clustering of these elements.

In the as-received specimen, the Y:Ti ratio of 0.54 ± 0.33 ([Table 4a](#)) is consistent with a range of 0.15–0.63 reported for other ODS alloys [8,9,28,36–42]. He, et al. [9] reported a Y:Ti ratio of 0.33 for the same heat of Fe-9%Cr ODS alloy in the present study. The Y:Ti ratio remained stable with proton irradiation (0.53 ± 0.26), but increased to 0.97 ± 0.81 upon neutron irradiation. The (Y+Ti):O ratio was also calculated for each condition ([Table 4a](#)). The as-

received (Y+Ti):O ratio of 1.16 ± 0.22 is consistent with He's [9] measurement of 1.4 on the same heat of Fe-9%Cr ODS and a range of $\sim 1\text{--}1.4$ reported for other ODS alloys [8,36–40,42]. The (Y+Ti):O ratio was relatively unchanged by proton (1.15 ± 0.31) or neutron (1.22 ± 0.46) irradiation. The Y:Ti and (Y+Ti):O ratios are plotted for each condition in [Figure 13](#).

Interestingly, the cluster compositions ([Table 4b](#)) of the base oxide elements Y, Ti, and O are statistically constant across all three conditions, with only a slight decrease in Ti and O in the neutron-irradiated sample. A decrease in Ti composition of the clusters would explain the increase in the Y:Ti ratio, while a slight decrease in O composition of the clusters would also explain how the (Y+Ti):O ratios remained relatively consistent. The cluster composition of Si, Mn, and Ni all increase as a result of both irradiations, which is consistent with the visual evidence of clustering. Correspondingly, the matrix composition increases for Y, Ti, and O, indicating that more of these atoms have entered solution, while that of Si decreases slightly, further supporting the evidence that Si is clustering. The small quantities of Mn and Ni in the matrix appear to remain relatively flat.

Care should be taken when drawing conclusions solely from the composition data of [Table 4b](#). This is because the % composition of one element is also dependent upon the relative amounts of the other elements present. Take for example the matrix composition of Cr. From [Table 4b](#), it appears that the matrix composition of Cr has decreased upon irradiation, particularly for the neutron-irradiated sample. Based on this, one might conclude that the Cr atoms may have segregated elsewhere such as grain boundaries, carbides, or as α' precipitates. However, following neutron-irradiation, the matrix composition of Y, Ti, and O have increased, which would naturally have the net effect of decreasing the matrix composition of Cr, even if the same amount of Cr atoms remain in the matrix. Another way to evaluate the Cr trend upon

irradiation would be to compare the difference between the % in clusters for Cr (f_{cl}^{Cr}) and the overall volume fraction (f_v) of clusters (i.e. the relative enrichment) as is plotted in Figure 13. This enrichment has increased from 1.0% to 2.1% following proton-irradiation, while remaining flat following neutron-irradiation. The Cr is more likely segregating towards the oxides upon proton-irradiation.

These APT results show notable differences in nanocluster chemistry between each condition studied. The optimized APT analysis parameters in Table 2 provide a cursory indication of the differences in the clustering of the oxide elements. The d_{max} and N_{min} parameters for the as-received, proton-irradiated and neutron-irradiated conditions converged on different values independently, which indicates that the chemistry of the nanoclusters and surrounding matrix has evolved. Upon review of the measurements of the nanocluster size, density, and chemistry in Tables 4a-4b and Figures 11-13, it can be seen that this is in fact the case. This further emphasizes that optimization of d_{max} and N_{min} is necessary for every sample. It is not always appropriate to use the same d_{max} and N_{min} across all conditions for experimental control, as this may counter-intuitively lead to spurious measurement or detection of clusters.

4 Discussion

Microstructure measurements from TEM and APT enable the comparison of irradiation effects in the Fe-9%Cr ODS alloy across proton ($\sim 10^{-5}$ dpa/sec) and neutron ($\sim 10^{-7}$ dpa/sec) irradiations carried out to a fixed dose and temperature of 3 dpa at 500°C. As presented in the preceding Section 3, the size and number density of both voids and dislocation loops are similar

between the proton and neutron irradiations. But conversely, nanocluster evolution differed between proton and neutron irradiations. In order to gain insight into the mechanisms driving these variable microstructure results, the difference in dose rate between proton and neutron irradiations is considered first.

Mansur [43,44] theorized a temperature shift is necessary in order to produce consistent microstructures when the irradiation dose rate increases. The desired microstructures are bound by two mechanisms of point defect loss: (1) mutual recombination in the matrix, and (2) diffusion to sinks. The temperature shift for recombination-dominant and diffusion-dominant regimes is calculated for a reference condition of 500°C at 10^{-7} dpa/sec (Figure 14), conditions comparable to the neutron irradiation experiment in the present study. The vacancy migration and formation energies are taken to be 0.55 eV and 2.25 eV, respectively, for a b.c.c. Fe-9%Cr steel [45]. But since the temperature is fixed at both dose rates in the present irradiation experiments, the temperature shift curve must have a slope ~ 0 in order for the proton- and neutron-irradiated void and dislocation loop microstructures to be consistent with one another, as observed in this work. It thus follows that void and loop nucleation and growth are recombination-driven processes (solid line, Figure 14), so their evolution will be relatively independent of dose rate at a fixed temperature.

Conversely, the evolution of oxide and Si-Ni-Mn nanoclusters is inconsistent between neutron and proton irradiations, suggesting that cluster formation and dissolution may not be recombination-driven processes. Multiple authors [46–48] have hypothesized that oxide nanocluster stability is governed by a balance between two competing effects: (1) ballistic dissolution due to irradiation damage cascades, and (2) thermal diffusion driving solute atoms to re-form into clusters (i.e. Ostwald ripening). In other words, solute atoms which de-cluster due to

impacts of irradiation damage cascades will more effectively diffuse back to the cluster at higher temperatures. Whereas at lower temperatures, there is insufficient energy to enable re-clustering, leaving some of the de-clustered atoms in solution. In the present study, both proton and neutron irradiations were carried out at the same temperature, 500°C, and to approximately the same dose, 3 dpa, yet the resulting particle size distributions (Figure 11), volume fraction of clusters (Table 4a) and the % enrichment of Y, Ti, O, Si, Mn, and Ni (Figure 12), are markedly different between the two irradiations. These observed differences in clustering are therefore ascribed to two mechanisms: first, the proton irradiation involved a higher dose rate (Figure 14) which would result in increased diffusivities for solute atoms and favor recombination or even Ostwald ripening; and second, proton and neutron irradiation are known to have differences in the nature of the ballistic impacts and the resultant cascade morphologies [49]. While protons create several small cascades, neutrons create a larger cascade [47,48], the volume of which is more likely to encompass a nanocluster susceptible to impact and eventual disordering or dissolution. This is further evidenced by the particle size distribution of the clusters after neutron-irradiation (Figure 11c), which exhibits a bimodal size distribution. Several authors [27,50,51] have suggested that a bimodal distribution may be indicative of cluster dissolution. It is hypothesized that solute atoms that have been ejected into solution may be starting to re-nucleate into smaller clusters, which would explain the higher population of clusters that are ~2 nm in diameter.

It should be noted that the temperature dependence of oxide nanocluster stability remains not well understood. Results of previous studies on this subject are summarized in Table 5. While several studies observed oxide dissolution upon irradiation [5,8,12,27,52–55] with increased stability at higher temperatures [5,8], others have reported oxide stability or even slight coarsening upon irradiation [5,6,9,28–30,40,56–64]. However, all of these data were collected

under inconsistent experimental conditions, including different irradiation temperatures, doses, irradiating particles, and using various analysis methods (i.e. TEM versus APT). Lescoat, et al. [28] conducted an experiment to isolate the effects of temperature alone (without irradiation) on a similar ODS alloy (Fe18Cr-Y₂O₃) by annealing a sample of the alloy for 1 hour at 1300°C. Lescoat observed oxide coarsening, indicative of the Ostwald ripening mechanism. However, in the present study, neutron irradiation at 500°C resulted in a reduction in average nanocluster size (with a bimodal size distribution), which is opposite of the ripening mechanism. This suggests that even in the presence of thermally-driven Ostwald ripening, the ballistic dissolution effects from irradiation are likely more dominant.

In the following sections, the observed irradiation evolution of the nanocluster chemistries is examined in greater detail. First, the change in composition of the oxide nanoclusters is addressed. Next, the nucleation of Ni, Mn, and Si-rich clusters is discussed.

4.1 Oxide Nanocluster Composition

Accompanying the partial dissolution of oxide nanoclusters is a change in their composition. In the present study, the Y:Ti ratio remains stable under proton irradiation, but increases from 0.54 to 0.97 under neutron irradiation. Other authors have measured similar irradiation-induced increases in the Y:Ti ratio. He, et al. [8] found the Y:Ti ratio to increase from 0.43 to 1.1 in 14YWT irradiated with Ni²⁺ ions at 300°C. Lescoat, et al. also reported an increase in the Y:Ti ratio in an Fe-18%Cr ODS alloy upon Fe⁺ ion irradiation at 500°C [28]. He

[9], in another study, also found the Y:Ti ratio to increase following 400°C proton irradiation of the identical Fe-9%Cr ODS alloy in the present study.

In the case of both proton and neutron irradiation, there is likely to be a ballistic dissolution process occurring with the oxide nanoclusters. The different bond energies for the Y_2O_3 and TiO_2 oxides may be compared. The enthalpies of formation for Y_2O_3 and TiO_2 are -1907 kJ/mol and -889 kJ/mol, respectively [65]. As a result, the yttrium will likely have a higher affinity for oxygen, causing the Y-O bond strength to be greater than the Ti-O bonds in the nanoclusters. Note that the exact structure of the nanoclusters may not, however, be a simple mixture of Y_2O_3 and TiO_2 . In addition, the estimated displacement energy, E_d , of Y is 57 eV [27,66,67], while the estimated displacement energy of Ti within an iron matrix is estimated to be only 30 eV [68]. Therefore, both of these factors suggest that the titanium oxide bonds will break more readily than yttrium oxide bonds, releasing more Ti than Y atoms into solution. Monnet et al. [27,67] also corroborated that the oxides eject more Ti than Y atoms upon irradiation.

Given that the Y:Ti ratio remained constant under 500°C proton irradiation in this study, it is likely that for damage produced by smaller proton-induced cascades, enhanced thermal diffusion at 500°C enables de-clustered Ti atoms to return to clusters. This is supported by the ratio of the mean square diffusion displacement, $\overline{r^2}$, at 400°C to that at 500°C, which is ~0.3, suggesting that atoms diffuse more than three times the distance at 500°C than they do at 400°C. Such a higher atomic mobility supports the plausibility that de-clustered Ti could diffuse back to clusters at 500°C following proton irradiation.

An increasing Y:Ti ratio due to neutron irradiation confirms that more Ti atoms than Y atoms are entering solution. However, in the case of neutron irradiation, the larger damage cascades and/or reduced solute mobility may less favor recombination of the oxides resulting in more net dissolution. Since the ratio of (Y+Ti):O remains stable in all examined conditions, it is believed that O atoms are ejected from nanoclusters along with, and at a similar rate as, the Ti atoms. The (Y+Ti):O ratio was also measured to be relatively unaffected by 400°C proton irradiation in the same Fe-9%Cr ODS alloy [9] or by Ni²⁺ ion irradiations at 450°C and 600°C in 14YWT [8]. Coupled with the decrease in the % of all Ti in clusters (Table 4a) and the Ti cluster composition (Table 4b) upon neutron irradiation, the Y:Ti and (Y+Ti):O ratios provide further evidence that the ballistic impacts of neutron irradiation have a greater dissolution effect than that of proton irradiation.

4.2 Si, Mn, and Ni Clusters

The clustering of Si, Mn, and Ni is a notable irradiation-induced chemistry change. The formation of similar clusters containing Si, Mn, and Ni are often reported in ferritic-martensitic (F-M) steels such as T91, HCM12, and HT9, and austenitic stainless steels [69–73], but rarely reported in ODS steels. Several cluster formation mechanisms have been proposed:

- a) Si, Mn, and Ni form oxide phases such as SiO₂, Mn₃O₄, or NiO and nucleate in conjunction with the existing oxide phases.
- b) Si, Mn, and Ni form silicides such as Mn₄Si₇, or Ni₃Si₂ and nucleate as their own precipitates independent of the existing oxides.

- c) Si, Mn, and Ni diffuse towards sinks (such as oxides) due to radiation-induced segregation (RIS).

The first possible mechanism was considered by Williams et al. [32], who observed clustering of Mn and Si in ODS-Eurofer 97 steel. The enthalpy of formation of the Fe, Cr, Y, Ti, Si, Mn, and Ni oxides relevant for Fe-9%Cr ODS are provided in [Table 6](#) [65]. It is clear from [Table 6](#) that all of these elements have a high affinity for oxygen, with the Si and Mn having enthalpy of oxide formation on the same order as that of Fe, Cr, and Ti. Yet, Si, Mn, and Ni oxides or clusters are not present in the as-received condition; their clustering is radiation-induced. In addition, the oxide formation mechanism does not explain why Si, Mn, and Ni also cluster upon irradiation in other F-M and austenitic stainless steels [69–71,73], which do not contain pre-existing oxide compounds. Therefore, this is not likely to be the primary mechanism of Si, Mn, and Ni clustering.

The second possibility considered is that the Mn and Ni form silicide compounds and precipitate out of solution. The enthalpy of formation of the relevant silicides for Fe-9%Cr ODS and commercial F-M steels are presented in [Table 7](#). Although all of these silicides have a negative enthalpy of formation, these enthalpies are less favorable than those of the oxides ([Table 6](#)). Furthermore, if silicide formation were the primary mechanism for Si, Mn, and Ni clustering in ODS and F-M steels, it would be expected that Mo would also cluster in other F-M steels due to the negative Mo silicide formation enthalpy, yet this has not been observed in irradiated F-M alloys [69–71,73]. Thus, silicide formation is not likely the primary mechanism of Si, Mn, and Ni clustering in ODS and F-M steels.

Finally, the possibility of RIS is considered as the driving mechanism for Si, Mn, and Ni clustering. As shown in [Table 4b](#), Si, Mn, and Ni are found in higher concentrations within the

oxides following proton and neutron irradiation. The enrichment of Si, Mn, and Ni in the nanoclusters is illustrated in [Figure 12](#). Si, Mn, and Ni are known to segregate toward grain boundaries in commercial F-M and austenitic stainless steels [73–75]. Thus, the RIS mechanisms reported in literature appear to be consistent with the solute enrichments at oxides observed in this study, suggesting that the clustering of Si, Mn, and Ni is the likely result of RIS toward existing point defect sinks within the matrix, such as oxide nanoclusters.

5 Conclusions

In this study, Fe-9%Cr ODS specimens were irradiated with protons to 3 dpa at 500°C and separate specimens were irradiated with neutrons also to 3 dpa at 500°C. The microstructure of each specimen was then characterized with TEM and APT and compared to the microstructure of the original as-received sample. The results of the proton irradiation were evaluated to consider whether proton irradiation is an adequate surrogate for neutron irradiation. Some similarities and differences were observed and reported:

- 1) The average size and number density of dislocation loops and voids were similar in both proton- and neutron-irradiated specimens. It therefore follows that proton irradiation can likely reproduce the microstructure evolution of neutron irradiation for these recombination-driven processes.
- 2) The radiation stability of the oxide nanoclusters was notably different between proton- and neutron-irradiated specimens. Oxides exhibited limited stability under proton irradiation, while their size and number density both decreased, and their Y:Ti ratio

increased, following neutron irradiation. The (Y+Ti):O ratio of the clusters was unchanged by both proton and neutron irradiations. These differences in oxide evolution are rationalized by two competing factors: (a) differences in diffusion arising from differences in the irradiation dose rate, and (b) differences in the ballistic effects of the irradiating particles.

- 3) Si, Mn, and Ni clustered at the oxides in both proton- and neutron-irradiated specimens. These clusters are likely attributed to the same mechanisms driving RIS of these elements toward point defect sinks in bcc Fe-Cr alloys.

This study also demonstrated the importance of appropriately selecting the d_{max} parameter for conducting cluster analysis of APT data using IVAS 3.6.2. A new d_{max} should be determined for each specimen condition, considering the possibility that the composition of the matrix has been altered as a result of irradiation. The d_{max} should be chosen at a position at or near the trough of the cluster count vs. d_{max} curve to minimize the amount of spuriously detected clusters that can inflate the size and number density estimates.

Proton irradiation provides a meaningful simulation of the recombination-driven microstructural processes, such as dislocation loop and void nucleation and growth, resulting from neutron irradiation at a fixed dose and temperature. However, the irradiation response of oxide and Si-Mn-Ni-rich nanoclusters differs between neutron and proton irradiation. The mechanisms governing nanocluster evolution are sensitive to differences in diffusion and ballistic effects, and thus proton irradiation produces varying nanocluster behaviors than does neutron irradiation at a fixed dose and temperature.

Acknowledgements

The authors thank J. Burns and Y.Q. Wu in the Microscopy and Characterization Suite (MaCS) at the Center for Advanced Energy Studies (CAES). The authors also acknowledge G.S. Was, O. Toader, and F. Naab at the University of Michigan for their assistance with proton irradiations. This research was sponsored in part by the US Nuclear Regulatory Commission Grant NRC-HQ-84-14-G-0056 and by the US DOE, Office of Nuclear Energy under DOE Idaho Operations Office Contract DE-AC07-05ID14517, as part of ATR National Scientific User Facility experiment 14-486.

Tables and Figures

Table 1. Chemical Composition of Fe-9%Cr ODS

Chemical Composition (wt%, balance Fe)														
C	Si	Mn	P	S	Ni	Cr	W	Ti	Y	O	N	Ar	Y ₂ O ₃	Ex. O
0.14	0.048	0.05	<0.005	0.004	0.06	8.67	1.96	0.23	0.27	0.14	0.017	0.004	0.34	0.07
[Y ₂ O ₃] = 1.27 x [Y]														
[Ex.O] = [Total O] – [O in Y ₂ O ₃ powder] = [O] – 0.27 x [Y]														

Table 2. Summary of analysis parameters used for the APT cluster analysis of Fe-9%Cr ODS

Parameter	As-received	Proton-irradiated (3 dpa, 500°C)	Neutron-irradiated (3 dpa, 500°C)
$d_{\max}$ (nm)	0.9-1.1	0.9	0.7
$N_{\min}$	8	8	8
d_{sur} (nm)	0.5	0.5	0.5
d_{er} (nm)	0.2	0.2	0.2

Table 3. Summary of microstructural measurements from TEM.

Feature	Measurement	As-received	Proton-irradiated (3 dpa, 500°C)	Neutron-irradiated (3 dpa, 500°C)
Grains/Laths	# of grains measured	104	104	104
	Effective diameter ($\times 10^{-6}$ m)	0.23 ± 0.12	0.31 ± 0.11	0.31 ± 0.09
Dislocation lines	# of measurements	17	46	39
	Density ($\times 10^{14}$ m $^{-2}$)	19.1 ± 3.8	17.6 ± 5.3	18.5 ± 4.8
Carbide Precipitates	# of carbides measured	36	51	68
	Effective diameter ($\times 10^{-6}$ m)	0.11 ± 0.07	0.07 ± 0.03	0.10 ± 0.06
	Density ($\times 10^{20}$ m $^{-3}$)	0.20	0.46	0.47
Voids	# of voids measured	0	8	22
	Diameter ($\times 10^{-9}$ m)	-	4.00 ± 1.51	3.64 ± 1.14
	Density ($\times 10^{21}$ m $^{-3}$)	-	0.34 ± 0.44	0.24 ± 0.12
Dislocation loops	# of loops measured	0	688	182
	Diameter ($\times 10^{-9}$ m)	-	8.4 ± 1.7	8.9 ± 2.0
	Density ($\times 10^{21}$ m $^{-3}$)	-	10.2 ± 8.0	2.7 ± 0.7

Table 4a. Summary of oxide nanocluster measurements for as-received, proton-irradiated and neutron-irradiated conditions, with the % of clustering for each species, Y:Ti, and (Y+Ti):O.

Oxide nanoclusters	As-Received	Proton-irradiated (3 dpa, 500°C)	Neutron-irradiated (3 dpa, 500°C)
# of clusters measured, ΣN_c	486	964	335
Analysis Volume, V_T (nm ³)	856,053	1,722,204	816,586
Average Diameter, D_G (nm)	5.96	4.77	3.41
Standard deviation for D_G	± 3.10	± 1.91	± 1.69
Std. dev. of the mean for D_G	± 0.14	± 0.06	± 0.09
Density, N_{nc} (x 10 ²¹ m ⁻³)	568	560	435
Volume fraction, f_v	5.2%	5.1%	2.4%
Species, % in clusters, f_{cl}^i			
Y	74.0%	81.3%	52.1%
Ti	71.4%	65.5%	24.0%
O	66.2%	67.7%	32.3%
Cr*	6.2%	7.3%	3.4%
Si	7.1%	11.1%	8.3%
Mn	5.9%	6.8%	6.0%
Ni	8.1%	16.8%	8.3%
C*	10.6%	13.5%	4.5%
W*	5.1%	3.2%	1.8%
*Does not include species clustering in carbide precipitates			
Y:Ti	0.54 ± 0.33	0.53 ± 0.26	0.97 ± 0.81
(Y+Ti):O	1.16 ± 0.22	1.15 ± 0.31	1.22 ± 0.46

Table 4b. Summary of cluster and matrix composition measurements for as-received, proton-irradiated and neutron-irradiated conditions

Oxide nanoclusters	As-received	Proton-irradiated (3 dpa, 500°C)	Neutron-irradiated (3 dpa, 500°C)
Cluster composition (at. %)			
Y	(2.41±1.24)%	(2.43±1.31)%	(2.93±1.85)%
Ti	(4.77±1.75)%	(4.64±1.74)%	(3.75±2.28)%
O	(6.25±3.49)%	(6.24±3.14)%	(5.85±4.45)%
Cr	(9.78±2.08)%	(11.80±2.52)%	(10.55±3.25)%
Si	(0.19±0.17)%	(0.30±0.23)%	(0.38±0.49)%
Mn	(0.07±0.10)%	(0.08±0.12)%	(0.19±0.30)%
Ni	(0.04±0.08)%	(0.10±0.10)%	(0.13±0.23)%
C	(0.27±0.30)%	(0.25±0.25)%	(0.28±0.45)%
W	(0.58±0.39)%	(0.37±0.30)%	(0.58±0.62)%
Matrix composition (at. %)			
Y	0.05%	0.04%	0.10%
Ti	0.11%	0.15%	0.32%
O	0.17%	0.19%	0.37%
Cr	8.38%	8.21%	8.14%
Si	0.15%	0.13%	0.12%
Mn	0.06%	0.06%	0.08%
Ni	0.03%	0.03%	0.05%
C	0.15%	0.12%	0.16%
W	0.61%	0.60%	0.66%
Trace amounts of P, S, N and H, Ga detected (balance is Fe)			

Table 5. A comparison of literature studies evaluating the stability of oxide nanoclusters upon irradiation.

Reference	Alloy(s)	Radiation Type	Dose (dpa)	Irradiation Temperature (°C)	Analysis Method	Reported oxide trend (size and density evolution)
APT-based Analysis						
This study	Fe-9%Cr ODS	2 MeV protons	3	500	APT	Slight oxide dissolution
This study	Fe-9%Cr ODS	Fast neutrons (ATR)	3	500	APT	Oxide dissolution
[8]	14YWT	5 MeV Ni ⁺⁺ ions	100	300-600	APT-TEM-STEM	More stable at high temperature
[5]	14YWT	2 MeV protons	1-3	400		Stable
[5]	14YWT	5 MeV Ni ⁺⁺ ions	5-100	-75-450	APT-TEM-EFTEM	More stable at high temperature
[64]	MA957	Fast Neutrons (FFTF-MOTA)	109-113	412-670	APT	Stable
[28]	Fe-18Cr-Y ₂ O ₃	500 keV Fe ⁺ ions	74.4-150	500	APT-TEM	Slide coarsening
[9]	Fe-9%Cr ODS	2 MeV protons	3.7	400	APT-TEM-STEM-EDS	Slight coarsening
[62]	EUROFER97 ODS	150 keV Fe ions	10	300	APT	Stable
[5]	Fe-9%Cr ODS	Fast neutrons (ATR)	3	500	APT-TEM-EFTEM	Stable
[6]	Fe-9%Cr ODS	2.6 MeV protons	1	525	APT-TEM-EFTEM-STEM-EDS	Stable
[39]	12YWT	150 keV Fe ions	0.7	300	APT	Stable
TEM-based Analysis						
[52]	Fe-18Cr-1W-0.3Ti+0.6Y ₂ O ₃	150 keV Fe ⁺ ions	4-45	500	TEM-EFTEM-EELS-STEM-EDS	Smaller oxides are stable; larger oxides not stable
[53]	Model ODS steel	5 MeV Fe ions	25-100	500-600	TEM-SANS	Dissolution at high dose/temp.
[12]	F82H-ODS and High Cr-ODS	10.5 MeV Fe ³⁺ ions	20	250-380	TEM	Slight dissolution
[55]	Fe-9%Cr ODS	5 MeV Ni ⁺⁺ ions	5-150	500-700	TEM	Size decrease, density increase
[54]	MA957	Fast neutrons (JOYO)	44.5-101	502-709	TEM	Oxide dissolution
[27]	DY	Neutrons (Phenix)	30.5-79.3	435-580	TEM-STEM-EDS	Dissolution at higher doses
[27]	DY, EM10+Y ₂ O ₃ , EM10+MGO	1-1.2 MeV electrons	50-100	300-550	TEM-STEM-EDS	Dissolution (with 1.2 MeV only)
[61]	MA957	Neutrons (Phenix)	50-75	412-430	TEM-EFTEM-HRTEM	No significant changes
[58]	16Cr0.1Ti	6.4 MeV Fe ions	60	650	TEM-EDS	Stable
[60]	EUROFER97 ODS	590 MeV protons	0.3-2	40	TEM	Stable
[57]	19Cr-4.5Al ODS	Ions	20	300-700	TEM	No significant changes
[59]	K1 (19Cr) and K4 (19Cr-4Al)	6.4 MeV Fe ³⁺ ions	20-150	500-700	TEM-STEM	Stable
[63]	EUROFER97 ODS variants	590 MeV protons	0.3-2	40-350	TEM-HRTEM-WDXRF	Stable
[56]	9 Cr and 12 Cr ODS	Fast neutrons (JOYO)	2.5-15	330-500	TEM	Stable
[30]	F95 (12Cr) and M93 (9Cr)	Fast neutrons (JOYO)	2.5-15	397-534	TEM-HRTEM	Stable; slight coarsening
[27]	DY, EM10 + Y ₂ O ₃ , EM10+MgO	1 MeV Helium	0.05	400	TEM-STEM-EDS	Stable
[29]	1DS (11Cr) and 1DK (13Cr)	Fast neutrons (JOYO)	10.5-21	450-561	TEM-STEM-EDS	Stable; possible dissolution

Table 6. A comparison of enthalpy of formation for various oxide phases, from [65].

Element	Oxide Composition	ΔH_f^{298} (kJ/mol)
Fe	Fe ₃ O ₄	-1118
Cr	Cr ₂ O ₃	-1130
Y	Y ₂ O ₃	-1907
Ti	TiO ₂	-889
Si	SiO ₂	-911
Mn	Mn ₃ O ₄	-1388
Ni	NiO	-241
W	WO ₃	-839

Table 7. A comparison of enthalpy of formation for Mn, Ni, and Mo silicides, from [65].

Element	Silicide Composition	ΔH_f^{298} (kJ/mole)
Mn	Mn ₂ Si	-80
	Mn ₅ Si ₃	-201
	MnSi	-61
	Mn ₄ Si ₇	-309
Ni	Ni ₂ Si	-143
	Ni ₃ Si ₂	-232
	NiSi	-90
	NiSi ₂	-94
Mo	Mo ₃ Si	-116
	Mo ₅ Si ₃	-310
	MoSi ₂	-132

a)

b)

Figure 1. a) pattern of raster-scanned proton beam during irradiations, and b) SRIM-2008 [21] calculation of damage profile for 2 MeV proton irradiation normal to Fe-9%Cr in “Quick Calculation (K-P)” mode.

Figure 2. Typical sample geometries as imaged via SEM in the FIB for a) TEM sample films and b) APT sample needles.

Figure 3. Typical plots of $d_{\max}$ vs. cluster count, and the selected values for $d_{\max}$ for a) as-received, b) proton-irradiated to 3 dpa at 500°C, and c) neutron-irradiated to 3 dpa at 500°C.

Figure 4. Bright field TEM images of the general microstructure for a) as-received, b) 3 dpa, 500°C, proton-irradiated, and c) 3 dpa, 500°C, neutron-irradiated Fe-9%Cr ODS.

Figure 5. Representative voids in Fe-9%Cr ODS following 3 dpa, 500°C proton irradiation at a) under-focus, b) in-focus, and c) over-focus, and following neutron irradiation at d) under-focus, e) in-focus, and f) over-focus.

Figure 6. Representative dislocation loops in Fe-9%Cr ODS imaged along the [111] zone axis following a) proton irradiation and b) neutron irradiation, and c) dislocation loop diameter histogram.

Figure 7. Bright field TEM images of the oxide distributions for a) as-received, b) 3 dpa, 500°C, proton-irradiated, and c) 3 dpa, 500°C, neutron-irradiated Fe-9%Cr ODS.

Figure 8. APT atom distribution maps for as-received Fe-9%Cr ODS with software identified oxide clusters.

Figure 9. APT atom distribution maps for 3 dpa, 500°C, proton-irradiated Fe-9%Cr ODS, with software identified oxide clusters.

Figure 10. APT atom distribution maps for 3 dpa, 500°C, neutron-irradiated Fe-9%Cr ODS, with software identified oxide clusters.

Figure 11. Nanocluster Guinier diameter distribution for a) as-received, b) 3 dpa, 500°C, proton-irradiated, and c) 3 dpa, 500°C, neutron-irradiated Fe-9%Cr ODS.

Figure 12. Irradiation evolution of the enrichment of atoms in clusters ($f_{cl}^i - f_v$) for several different species.

Figure 13. Irradiation evolution of Y:Ti and (Y+Ti):O ratios.

Figure 14. Comparison of calculated temperature shifts required for diffusion-driven (dashed line) and recombination-driven (solid line) mechanisms to produce consistent microstructures, from [43,44].

References

- [1] S.J. Zinkle, J.T. Busby, *Mater. Today* 12 (2009) 12.
- [2] T. Allen, J. Busby, M. Meyer, D. Petti, *Mater. Today* 13 (2010) 14.
- [3] P. Yvon, F. Carré, *J. Nucl. Mater.* 385 (2009) 217.
- [4] L. Barnard, G.R. Odette, I. Szlufarska, D. Morgan, *Acta Mater.* 60 (2012) 935.
- [5] A. Certain, S. Kuchibhatla, V. Shutthanandan, D.T. Hoelzer, T.R. Allen, *J. Nucl. Mater.* 434 (2013) 311.
- [6] A.G. Certain, K.G. Field, T.R. Allen, M.K. Miller, J. Bentley, J.T. Busby, *J. Nucl. Mater.* 407 (2010) 2.
- [7] P. Dubuisson, Y. De Carlan, V. Garat, M. Blat, *J. Nucl. Mater.* 428 (2012) 6.
- [8] J. He, F. Wan, K. Sridharan, T.R. Allen, A. Certain, V. Shutthanandan, Y.Q. Wu, *J. Nucl. Mater.* 455 (2014) 41.
- [9] J. He, F. Wan, K. Sridharan, T.R. Allen, A. Certain, Y.Q. Wu, *J. Nucl. Mater.* 452 (2014) 87.
- [10] C. Hin, B.D. Wirth, *J. Nucl. Mater.* 402 (2010) 30.
- [11] R.L. Klueh, D.R. Harries, *High-Chromium Ferritic and Martensitic Steels for Nuclear Applications*, ASTM, 2001.
- [12] C. Liu, C. Yu, N. Hashimoto, S. Ohnuki, M. Ando, K. Shiba, S. Jitsukawa, *J. Nucl. Mater.* 417 (2011) 270.
- [13] H. Sakasegawa, L. Chaffron, F. Legendre, L. Boulanger, T. Cozzika, M. Brocq, Y. de Carlan, *J. Nucl. Mater.* 384 (2009) 115.
- [14] G.S. Was, J.T. Busby, T. Allen, E.A. Kenik, A. Jenssen, S.M. Bruemmer, J. Gan, A.D. Edwards, P.M. Scott, P.L. Andresen, *J. Nucl. Mater.* 300 (2002) 198.
- [15] J.M. Hyde, E.A. Marquis, K.B. Wilford, T.J. Williams, *Ultramicroscopy* 111 (2011) 440.
- [16] R.P. Kolli, D.N. Seidman, *Microsc. Microanal.* 13 (2007) 272.
- [17] P.D. Styman, J.M. Hyde, K. Wilford, G.D.W. Smith, *Ultramicroscopy* 132 (2013) 258.
- [18] D. Vaumousse, A. Cerezo, P.J. Warren, *Ultramicroscopy* 95 (2003) 215.

- [19] C.A. Williams, D. Haley, E.A. Marquis, G.D.W. Smith, M.P. Moody, *Ultramicroscopy* 132 (2013) 271.
- [20] S. Ohtsuka, S. Ukai, M. Fujiwara, T. Kaito, T. Narita, *Mater. Trans.* 46 (2005) 487.
- [21] J.F. Ziegler, J.P. Biersack, *SRIM - The Stopping and Range of Ions in Matter*, 2008.
- [22] R.E. Stoller, M.B. Toloczko, G.S. Was, a. G. Certain, S. Dwaraknath, F. a. Garner, *Nucl. Instruments Methods Phys. Res. Sect. B Beam Interact. with Mater. Atoms* 310 (2013) 75.
- [23] T. Allen, F. Marshall, J. Ulrich, eds., *ATR National Scientific User Facility 2012 Annual Report*, 2012.
- [24] C.M. Parish, K.G. Field, A.G. Certain, J.P. Wharry, *J. Mater. Res.* 30 (2015) 1275.
- [25] B. Yao, D.J. Edwards, R.J. Kurtz, *J. Nucl. Mater.* 434 (2013) 402.
- [26] K. Thompson, D. Lawrence, D.J. Larson, J.D. Olson, T.F. Kelly, B. Gorman, *Ultramicroscopy* 107 (2007) 131.
- [27] I. Monnet, P. Dubuisson, Y. Serruys, M.O. Ruault, O. Kaitasov, B. Jouffrey, *J. Nucl. Mater.* 335 (2004) 311.
- [28] 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, *Acta Mater.* 78 (2014) 328.
- [29] S. Yamashita, *J. Nucl. Mater.* 311 (2002) 283.
- [30] S. Yamashita, N. Akasaka, S. Ohnuki, *J. Nucl. Mater.* 329-333 (2004) 377.
- [31] M.K. Miller, R. Forbes, *Atom Probe Tomography: The Local Electrode Atom Probe*, Springer, New York, 2014.
- [32] C.A. Williams, E.A. Marquis, A. Cerezo, G.D.W. Smith, *J. Nucl. Mater.* 400 (2010) 37.
- [33] M. Bachhav, G. Robert Odette, E.A. Marquis, *Scr. Mater.* 74 (2014) 48.
- [34] C.A. Williams, G.D.W. Smith, E.A. Marquis, *Ultramicroscopy* 125 (2013) 10.
- [35] R.L. Scheaffer, J.T. McClave, *Probability and Statistics for Engineers*, Duxbury Press, Belmont, CA, 1995.
- [36] M.J. Alinger, G.R. Odette, D.T. Hoelzer, *Acta Mater.* 57 (2009) 392.
- [37] E.A. Marquis, *Appl. Phys. Lett.* 93 (2008) 181904.

- [38] M.K. Miller, K.F. Russell, D.T. Hoelzer, J. Nucl. Mater. 351 (2006) 261.
- [39] M.K. Miller, D.T. Hoelzer, E.A. Kenik, K.F. Russell, J. Nucl. Mater. 329-333 (2004) 338.
- [40] P. Pareige, M.K. Miller, R.E. Stoller, D.T. Hoelzer, E. Cadel, B. Radiguet, J. Nucl. Mater. 360 (2007) 136.
- [41] H. Sakasegawa, L. Chaffron, F. Legendre, M. Brocq, L. Boulanger, S. Poissonnet, Y. de Carlan, J. Bechade, T. Cozzika, J. Malaplate, J. Nucl. Mater. 386-388 (2009) 511.
- [42] M.K. Miller, E.A. Kenik, K.F. Russell, L. Heatherly, D.T. Hoelzer, P.J. Maziasz, 353 (2003) 140.
- [43] L.K. Mansur, J. Nucl. Mater. 78 (1978) 156.
- [44] L.K. Mansur, J. Nucl. Mater. 206 (1993) 306.
- [45] J.P. Wharry, G.S. Was, Acta Mater. 65 (2014) 42.
- [46] G. Martin, Phys. Rev. 30 (1984) 1424.
- [47] K.C. Russell, J. Nucl. Mater. 206 (1993) 129.
- [48] R.S. Nelson, J.A. Hudson, D.J. Mazey, J. Nucl. Mater. 44 (1972) 318.
- [49] G.S. Was, Fundamentals of Radiation Materials Science: Metals and Alloys, 2007.
- [50] H.J. Frost, K.C. Russell, Acta Metall. 30 (1982) 953.
- [51] A. Xu, C. Beck, D.E.J. Armstrong, K. Rajan, G.D.W. Smith, P. a. J. Bagot, S.G. Roberts, Acta Mater. 87 (2015) 121.
- [52] M.-L. Lescoat, J. Ribis, A. Gentils, O. Kaïtasov, Y. de Carlan, A. Legris, J. Nucl. Mater. 428 (2012) 176.
- [53] C. Robertson, B.K. Panigrahi, S. Balaji, S. Kataria, Y. Serruys, M.-H. Mathon, C.S. Sundar, J. Nucl. Mater. 426 (2012) 240.
- [54] S. Yamashita, N. Akasaka, S. Ukai, S. Ohnuki, J. Nucl. Mater. 367-370 (2007) 202.
- [55] T.R. Allen, J. Gan, J.I. Cole, M.K. Miller, J.T. Busby, S. Shutthanandan, S. Thevuthasan, J. Nucl. Mater. 375 (2008) 26.
- [56] N. Akasaka, S. Yamashita, T. Yoshitake, S. Ukai, A. Kimura, J. Nucl. Mater. 329-333 (2004) 1053.

- [57] A. Kimura, H.-S. Cho, N. Toda, R. Kasada, K. Yutani, H. Kishimoto, N. Iwata, S. Ukai, M. Fujiwara, J. Nucl. Sci. Technol. 44 (2007) 323.
- [58] H. Kishimoto, R. Kasada, O. Hashitomi, A. Kimura, J. Nucl. Mater. 386-388 (2009) 533.
- [59] H. Kishimoto, K. Yutani, R. Kasada, O. Hashitomi, A. Kimura, J. Nucl. Mater. 367-370 (2007) 179.
- [60] A. Ramar, N. Baluc, R. Schäublin, J. Nucl. Mater. 367-370 (2007) 217.
- [61] J. Ribis, S. Lozano-Perez, J. Nucl. Mater. 444 (2014) 314.
- [62] S. V Rogozhkin, T. V Kulevoy, N.A. Iskandarov, N.N. Orlov, B.B. Chalykh, A.A. Aleev, N.Y. Grachev, R.P. Kujbida, A.A. Nikitin, A.D. Fertman, At. Energy 114 (2013) 12.
- [63] R. Schäublin, A. Ramar, N. Baluc, V. de Castro, M.A. Monge, T. Leguey, N. Schmid, C. Bonjour, J. Nucl. Mater. 351 (2006) 247.
- [64] N.A. Bailey, E. Stergar, M. Toloczko, P. Hosemann, J. Nucl. Mater. 459 (2015) 225.
- [65] W. Gale, T. Totemeier, Smithells Metals Reference Book, eighth ed., Elsevier, 2004.
- [66] M.D. Rechtin, H. Wiedersich, Radiat. Eff. 31 (1977) 181.
- [67] I. Monnet, T. Van den Berghe, P. Dubuisson, J. Nucl. Mater. 424 (2012) 204.
- [68] ASTM E521, Standard Practice for Neutron Radiation Damage Simulation by Charged-Particle Irradiation, ASTM International, West Conshohocken, PA, 2003.
- [69] Z. Jiao, G.S. Was, Acta Mater. 59 (2011) 4467.
- [70] Z. Jiao, G.S. Was, J. Nucl. Mater. 425 (2012) 105.
- [71] Z. Jiao, G.S. Was, J. Nucl. Mater. 449 (2014) 200.
- [72] S.C. Glade, B.D. Wirth, G.R. Odette, P. Asoka-Kumar, J. Nucl. Mater. 351 (2006) 197.
- [73] J.P. Wharry, Z. Jiao, V. Shankar, J.T. Busby, G.S. Was, J. Nucl. Mater. 417 (2011) 140.
- [74] J.P. Wharry, G.S. Was, J. Nucl. Mater. 442 (2013) 7.
- [75] J.P. Wharry, Z. Jiao, G.S. Was, J. Nucl. Mater. 425 (2012) 117.