Microchemical and microstructural evolution of AISI 304 stainless steel irradiated in EBR-II at PWR-relevant dpa rates

Yan Dong¹, B. H. Sencer², F. A. Garner³, E. A. Marquis^{1*}

1 – Department of Materials Science and Engineering, University of Michigan, Ann Arbor MI 48109, USA

2 – Idaho National Laboratory, Idaho Falls, ID 83402, USA

3 - Radiation Effects Consulting, Richland, WA 99354, USA

*Corresponding author:

Tel: (734) 764-8717

Email: emarq@umich.edu

Abstract

AISI 304 stainless steel was irradiated at 416°C and 450°C at a 4.4×10^{-9} and 3.05×10^{-7} dpa/s to ~0.4 and ~28 dpa, respectively, in the reflector of the EBR-II fast reactor. Both unirradiated and irradiated conditions were examined using standard and scanning transmission electron microscopy, energy dispersive spectroscopy, and atom probe tomography on very small specimens produced by the focused ion beam milling. These results are compared with previous electron microscopy examination of 3 mm disks from essentially the same material. By comparing a very low dose specimen with a much higher dose specimen, both derived from a single reactor assembly, it has been demonstrated that the coupled microstructural and microchemical evolution of dislocation loops and other sinks begins very early, with elemental segregation producing at these sinks what appears to be measurable precursors to fully formed precipitates found at higher doses. The nature of these sinks and their possible precursors are examined in detail.

Keywords: 304 stainless steel, neutron irradiation, void swelling, precipitation, segregation, atom probe tomography

1. Introduction

AISI 304 stainless steel was used to construct most components of the sodium-cooled EBR-II fast reactor. It was also used for the internal components of boiling water reactors (BWRs) and pressurized water reactors (PWRs) currently operating to produce electricity. Exposure of this steel and other austenitic stainless steels to neutron irradiation inevitably leads to a degradation of mechanical properties and dimensional instability arising from void swelling, irradiation creep, and phase evolution [1-4]. While corrosion and cracking of this steel are not very significant issues in sodium coolant, they are much more important in water coolant, however, requiring a greater focus on radiation-induced segregation and microchemical evolution in PWRs and BWRs, especially with respect to their impact on irradiation-assisted stress corrosion cracking [5, 6].

Within the core of EBR-II, it was possible to attain ~ 7 -15 dpa per year, but in PWRs the damage rate in the core internals is a maximum of ~ 2 dpa/year, occurring adjacent to the outermost fuel elements which are separated from the steel internals by a very small water gap, with the dpa rate decreasing strongly as one moves away from the core into the baffle-former assembly [3, 4]. BWRs have a much larger water gap between the outermost fuel element and the shroud, resulting in much lower damage rates experienced by the steel [4]. However, there is very little material available from BWRs and especially from PWRs that can be used to study the microchemical and microstructural evolution of the steel in response to neutron irradiation at elevated temperatures.

With the exception of test specimens irradiated in various reactors such as BOR-60 [7], Phénix and OSIRIS [8], and BR-2 [9], most of the insight on radiation damage in this steel has been generated using data derived from examination of structural components and test specimens irradiated in EBR-II [10-20]. For many years, the focus of these studies was primarily on void swelling and irradiation creep, and secondarily on phase instabilities, which are not as pronounced in 304 stainless steel compared to other austenitic steels such as AISI 316. Most of these studies in the late 1970s to early 1990s involved relatively high doses (10-100 dpa) and did not focus strongly on the early microchemical processes, partially because it was then thought not to be very important, but also because the analytical tools available then were not sophisticated enough to image the fine microchemical structure evolving at low dose.

With the availability of new techniques such as focused ion beam (FIB) milling of microscopy specimens and atom probe tomography (APT), it now is possible to examine many of the microchemical processes that are precursors to the onset of swelling and are occurring at very low dose. However, again only limited PWR or BWR material is available to examine, although a few recent studies have been published [21-25]. In this report we have chosen to examine AISI 304 irradiated at low dose rates in two reactor locations: within and far above the reflector region of EBR-II. A recently published study by Huang involving the same material at very closely adjacent locations to those used in our studies focused primarily on the microstructural evolution using conventional transmission electron microscopy on typical 3 mm disks [26]. Unfortunately, the intense radioactivity of the relatively large specimens precluded reliable microchemical analysis. In the current companion study we use much smaller FIB-produced specimens derived from the same source as Huang's specimens, and focus primarily on segregation and microchemical evolution of this same material, and secondarily we focus on microstructural evolution in order to allow comparison between the two studies to highlight the reproducibility as well as relative advantages and disadvantages of the two specimen production techniques.

2. Materials and techniques

The AISI 304 stainless steel examined in this study was the archived and unirradiated material in the form of a large hexagonal cross-section block and two neutron irradiated blocks, one at low dose and another at moderately high dose, with all three blocks produced from the same metallurgical heat and the same production run.

The irradiated material was cut from two of a series of five solid hexagonal cross-section blocks that were vertically stacked in a thin-wall hexagonal duct in Row 8 of EBR-II, the ensemble serving as a neutron reflector assembly. The blocks were ~52 mm flat-to-flat and had varying lengths averaging ~240 mm. The set of hexagonal blocks were irradiated to a mid-plane maximum of 33 dpa at a dose rate of 3.6×10^{-7} dpa/s.

Throughout the reflector assembly there were variations in dose rate depending on the location within the blocks, with the lowest dose reaching ~0.4 dpa. There were also variations in temperature arising from the local sodium coolant temperature and the local gamma heating rate,

the latter serving to elevate the temperature inside the block. These blocks have been used in a series of studies involving dimensional distortion, internal swelling profiles, microstructural evolution, density change, mechanical properties and ultrasonic velocity changes [26-33]. This study is the most recent in the series and used specimens taken from block #3 in the middle of the stack and from block #5, the highest in the stack.

The starting state of the blocks was somewhat unknown, since the original 50 year-old purchase order did not specify the final condition, but only the steel and its required dimensions. From previous work in this series, however, it was determined from microstructural examination that the archived material was ~5% cold worked in the block interior and ~10% cold worked near the block surfaces [26]. The alloy composition was measured in a previous study on an archive block by inductively coupled plasma atomic emission spectroscopy (ICP-AES) [27] and is listed in Table 1.

For the current study, thin plates of 0.04 cm thickness were cut from the mid-section of block #3 and from the top of block #5, using a diamond wafer saw, followed by further cutting and polishing to produce 3 mm diameter disks of 50-80 μm thickness. The block #3 specimens were irradiated to 28 dpa at 445°C at 3.05×10^{-7} dpa/s. We have confidence in the calculated temperature of this plate to only $\pm 10^\circ\text{C}$. The plate used in this study was archived as #3D1C1C, which was adjacent (within 0.08 cm) to one of the plates used by Huang [26], so the irradiation conditions are expected to be essentially the same as those cited by her. The estimated irradiation temperature and dose for specimens from block #5 are 416°C and 0.4 dpa, accumulated at 4.4×10^{-9} dpa/s. The plate used in this study was archived as #5D1C1B, which was immediately adjacent (within 0.04 cm) to one of the plates used by Huang [26], so the irradiation conditions are also expected to be essentially the same. We have confidence in the temperature assignment to $\pm 2-3^\circ\text{C}$ since the gamma heating rates are very low so far above the core and the coolant temperature is well known at that elevation. However, the dose assignment for block #5 is much less certain, having been derived by judgment and extrapolation based on many previous studies conducted in EBR-II, extrapolating from calculations made in earlier studies from the mid-block position of block #2 to the center of block #3 to the mid-block position of block #4. Therefore the assignment should be viewed as a nominal one only, but representative of a low-dose and low dose-rate position. Our best estimate is that the actual dose may be a factor of ~2 lower or higher.

The disks were ground on both sides on 1200 grit SiC paper. One side of the sample was then vibratory polished using 0.5 micron colloidal silica. The samples were then etched in 10% oxalic acid with 4V applied voltage for 15-30 seconds to reveal grain boundaries. The grain structures and types of grain boundaries were evaluated through electron back-scattered diffraction (EBSD) using a FEI Quanta 3D dual beam scanning electron microscope/focused ion beam (SEM/FIB) instrument. It was found that grain boundaries are mainly randomly-oriented high-angle grain boundaries with a few $\Sigma 3$ boundaries. Three randomly chosen high-angle grain boundaries were selected and analyzed by transmission electron microscopy (TEM) and APT. Both TEM foils and needle-shaped APT samples were prepared through the standard lift-out method using the focused ion beam technique.

TEM foils were studied using a FEI Tecnai G2 F30 STEM instrument. Chemical inhomogeneity in the matrix and grain boundary chemistry was characterized by STEM-EDS. Selected area diffraction and convergent beam diffraction (CBED) patterns were collected from the precipitates and indexed using JEMS software. The local sample thickness was estimated from EELS spectra.

The APT samples were analyzed using a CAMECA LEAP-4000XHR operated in laser pulsing mode with 200 kHz pulse repetition rate and 50-60 pJ laser energy. The temperature of the specimens was maintained at 50 K while the standing voltage was varied automatically to maintain a detection rate of 0.005-0.010 ions/pulse. The collected data were reconstructed and analyzed using the reconstruction software IVAS 3.6.6. The default values of k factor (3.3), image compression factor (1.65) and evaporation field of Fe (33V/nm) were selected for reconstruction. These parameters led to a reasonable reconstruction of the different microstructural features. For selected APT datasets, a cluster analysis was performed based on the nearest neighbor distribution method as described in [34].

3. Results

3.1 Unirradiated condition

As noted earlier, previous measurements indicated that the interior of the block material was about 5% cold worked [26] and our specimens were derived from interior positions. In this study,

a uniform distribution of alloying elements was observed in the matrix, with no evidence of clustering, precipitation or any compositional inhomogeneity, indicating that the final production treatment of the block probably involved full annealing prior to final deformation without thermal treatment thereafter, a common practice for production of such blocks. A representative dataset is shown in **Figure 1(a)**, but other areas produced the same results. The measured composition of the matrix (not taking into account grain boundary regions) is summarized in **Table 1**. The composition measured by APT agrees rather well with the composition previously determined by ICP-AES [27]. The lower sulfur content determined by APT is reasonable considering that S is usually found concentrated in sulfide precipitates and is therefore not easily measured in the APT technique. The $^{32}\text{S}^{2+}$ peak and the $^{16}\text{O}^{+}$ peak overlap at the mass-to-charge ratio of 16 Da in the APT mass spectra, creating an uncertainty in the detected species. There were no peaks at 16.5 Da ($^{33}\text{S}^{2+}$) or 33Da ($^{33}\text{S}^{+}$) that would have clarified the origin of the 16 Da peak, and the peak at 32 Da ($^{32}\text{S}^{+}$) overlaps with $^{64}\text{Ni}^{2+}$. Therefore the peak at 16 Da was assigned to $^{32}\text{S}^{2+}$. Small amounts of Co, Mo, V and Cu were also detected that were not reported in the ICP data.

Segregation of various alloying elements was observed at high angle grain boundaries, as shown in **Figure 1(b)**, where the segregation of P, B, C and Mo is evident and a slight segregation of Cr was also observed. Solute segregation was quantitatively evaluated by measuring Gibbsian interfacial excesses [35, 36] and values are listed in **Table 2**.

3.2 Neutron-irradiated conditions

Several microstructural features that were not present in the archive material were observed in the neutron-irradiated material. These include voids, second phase precipitates, dislocation loops, and stacking faults with segregation, and modified compositional profiles at grain boundaries.

Voids - As seen in **Figure 2**, the voids have the typical truncated octahedral shape with major facets lying on (111) planes. Void sizes were estimated from the diameter of spherical voids with the same projected area. From the size distributions in **Figure 2**, the average void sizes are 21.3 ± 5.2 nm and 26.0 ± 11.2 nm for the 0.4 dpa and 28 dpa samples respectively. In the 28 dpa material, the voids size range is larger than at 0.4 dpa with void sizes ranging from 5.2 nm to 54.4 nm. Since the void sizes are much smaller than the thickness of the TEM sample, the

observed size distribution is presented without a correction accounting for possible truncation of the voids at the specimen surface [37]. Based on the measured sample thickness, the number densities of voids are $(2.1 \pm 0.4) \times 10^{20} \text{ m}^{-3}$ and $(1.8 \pm 0.6) \times 10^{21} \text{ m}^{-3}$ for the 0.4 dpa and 28 dpa conditions respectively, where the uncertainty arising primarily from the error associated with foil thickness measurement by EELS. Swelling was estimated from the total volume of the voids divided by the volume of the sample, yielding a value of $0.13 \pm 0.03 \%$ for the 0.4 dpa condition and $2.8 \pm 0.8\%$ for the 28 dpa condition.

Precipitates – In the 0.4 dpa material (**Figure 3(a)**), near-spherical Ni and Si-rich precipitates were observed in the matrix with Nb at the center surrounded by Ni and Si. The Ni-to-Si ratio at the core is 4.0 ± 0.8 and higher in the shell (9.4 ± 2.8). The diameters of the precipitates (d_{ppt}) were defined by the FWHM of the Nb peak for the core that is $\sim 5 \text{ nm}$ and the (Ni+Si) concentration peak for the entire Ni and Si rich structure, which is $\sim 15 \text{ nm}$. The estimated precipitate number density is $(2.4 \pm 2.4) \times 10^{21} \text{ m}^{-3}$. The cited standard deviation is large due to the limited sampling in the relatively small APT datasets. In the 28 dpa material (**Figure 3(b)**), near-spherical Ni-Si clusters were also observed either as isolated entities or arranged on dislocation loops. The Ni-to-Si ratio is 3.0 ± 0.4 . Nb was observed in some of the isolated Ni-Si precipitates, but no evidence of Nb was found in the Ni-Si clusters that were associated with dislocation loops. The diameter of the clusters is $\sim 8 \text{ nm}$ and the number density is $(6.30 \pm 4.90) \times 10^{21} \text{ m}^{-3}$.

Phosphorus-rich platelets were observed in the 0.4 dpa material. High concentrations of nearly all major alloying elements were found in the vicinity of these precipitates (**Figure 4(a)**); however the distributions of Ni and Si are less concentrated and more diffuse than those of other segregating solutes (**Figure 4(b)-4(c)**). In the high dose condition, P-rich platelets were also observed but were smaller in size than those observed in the low dose condition (**Figure 5**), suggesting a reduction as other competing phases are formed at higher dose or different temperature. Coincidentally, the observed P-rich plates in the 0.4 dpa material are of comparable size with the plate defects observed by TEM. These plates are parallel to (111) planes with two different variants visible in **Figure 4(d)**.

Additional phases were observed for the 28 dpa material. An example of a non-spherical precipitate rich in Ni, Si and Mn with a slight enrichment in P and Nb is shown in **Figure 6**. These precipitates show a Ni-to-Si ratio of 2.4 ± 0.3 , consistent with the stoichiometry of the

$M_6Ni_{16}Si_7$ G phase, where the transition elements M are Cr or Mn [38, 39]. Small carbide precipitates were also occasionally observed in the matrix (**Figure 7**). The carbides were rich in Cr, C, V and Mo with small amounts of N. Segregation of Ni, Si and Co was also found at the carbide interface. The C-to-Cr ratio in the carbide was 0.25 ± 0.03 , which agrees with the stoichiometry of the $M_{23}C_6$ carbide phase.

Finally, ferrite phase was also observed in the high dose condition, as shown in **Figure 8(a)**. Segregation of Ni and Si was observed at the interface between the ferrite grain and the austenite matrix. Several other phases were observed near the ferrite grain, including a carbon and silicon-rich precipitate, denoted as carbon-silicide, a Ni and Si rich precipitate with comparable Ni/Si ratio, Mn enrichment, and shape as the G-phase shown in **Figure 6**, as well as three P-rich precipitates.

Dislocations– Dislocations were imaged using APT via the segregation of Ni and Si to their periphery (**Figure 9**). In both irradiation conditions, while enriched with Ni and Si, the dislocations were depleted with Cr and Mn with a slight P segregation observed for the 0.4 dpa condition. Very few dislocation loops were entirely contained in the datasets while several parts of larger and straighter loops were captured. In the 0.4 dpa condition, only two full loops were captured with diameters of ~ 20 nm and ~ 60 nm. In the 28 dpa condition, one full loop was observed with a diameter of ~ 40 nm. Note the numerous dislocation lines present in the 28 dpa condition. The dislocation line density, as defined by the total length of the dislocations per unit volume, was estimated to be $(2.6 \pm 1.8) \times 10^{14} \text{ m}^{-2}$ for the 0.4 dpa and $(6.5 \pm 2.0) \times 10^{14} \text{ m}^{-2}$ for the 28 dpa material, where the relatively large error is associated with the standard deviation from dataset to dataset.

Grain boundary chemistry – In the 0.4 dpa material, segregation of different solute species (Ni, Si, Co, Mo, V, Nb, P, C and B) was observed at randomly chosen high-angle grain boundaries (**Figure 10**). The Cr concentration profile usually exhibits a “W” shape, with an overall depletion over a width of about 25 nm and local segregation at the boundary plane relative to the immediate surrounding matrix. Ni, Co, and Si have significantly wider segregation peaks than the other segregating solutes (Cr, V, Mo, Nb, B). Small Cr, V, and Mo rich carbides with a C-to-Cr ratio of 0.23 ± 0.03 (**Figure 10(c)**) as well as P-rich precipitates were also observed along the same boundary (**Figure 10(d)**). Interfacial segregation, particularly of Ni, is evident at these two

precipitates. The Gibbsian interfacial excess for each segregating solute was calculated separately at locations 15 nm away from P-rich precipitates and at least 20 nm away from any precipitates. Results summarized in **Table 3** suggest that the grain boundary composition is affected by the presence of precipitates.

In the 28 dpa material, large precipitates identified as chromium carbides and carbo-silicides were observed on all of the randomly chosen high angle grain boundaries examined in this study (**Figure 11**). For chromium carbides, the overall C-to-Cr ratio is 0.25 ± 0.02 and the Cr-to-(Fe+Cr) ratio is 0.20 ± 0.02 . The carbides are also rich in Mo, V, P, B and N, while depleted in Co and Cu. Segregation of Ni and Si was confirmed at the interface between the carbide and the matrix. Nano-sized clusters of Fe and Ni were observed inside of the carbide (**Figure 11(e)**). Using cluster analysis, the average size of the clusters was determined to be ~ 2 nm in diameter, and the calculated number density of clusters in the carbide was $(3.5 \pm 0.1) \times 10^{18} \text{ cm}^{-3}$. The compositions of clusters and carbide matrix were measured separately and are listed in **Table 4**. The carbon-silicide phase is rich in Cr, Ni, C and Si. Unlike the Cr carbides, all elements are uniformly distributed inside these precipitates (**Figure 11(e)**). The two types of precipitates, regardless of their chemical composition, show the same electron diffraction pattern (**Figure 11(d)**), matching with the cubic structure of M_{23}C_6 carbide. In addition to carbides and carbon-silicides, one ferrite grain was also observed on one of the examined grain boundaries (**Figure 12**).

4 Discussion

Network dislocations - Previous TEM analysis by Huang on this material indicated that the unirradiated archive block contained a dislocation cell sub-structure typical of cold worked material [26], but the APT analysis did not find any solute clustering or segregation to line features, suggesting that either solute segregation to dislocations was negligible or that the dislocation density was too low to be detected by APT. As previously noted, if the material had been well annealed prior to the final cold working step, thermally-driven segregation would probably not have occurred.

Huang noted that this dislocation cell structure was not retained in the irradiated materials. Instead, dislocation loops were observed to dominate the microstructure. The removal of the dislocation network during irradiation and subsequent formation of high density of dislocation

loops has been observed in previous works [21, 24, 40, 41], although the exact mechanism of network removal has not yet been determined.

While our measured dislocation line densities are in general agreement with prior TEM measurements values for a range of steels and irradiation conditions compiled by Pokor et al., (between 2.8 and $14.6 \times 10^{14} / \text{m}^2$ calculated from reported loop densities between 13 and $63 \times 10^{21} / \text{m}^3$) [42], some discrepancy is noted between the results of this study and the results of Huang on essentially the same material. Using TEM, Huang showed that the line densities of the low dose and high dose specimens were essentially identical at 1.7 and $1.6 \times 10^{14} / \text{m}^2$, respectively, while the loops at the lower dose were larger (77.6 vs. 37 nm) and at lower densities (2.33 vs. $4.19 \times 10^{21} / \text{m}^3$), reflecting the expected behavior with varying dose rates. The APT measured line densities, taking into account all segregated line features, were larger and different at 3.5 and $6.5 \times 10^{14} / \text{m}^2$ for the low and high dose respectively. Therefore it is reasonable to assume that while APT can quantify chemistry, segregation, and the spatial correlation of loops and precipitates, the limited statistics and smaller volumes involved seem to produce a much larger uncertainty in size and density information than the TEM results. In particular, the limited structural information contained in the APT dataset does not allow distinguishing Frank loops from perfect loop configurations. It is also possible that the size and density differences are the result of randomly sampling a non-typical small volume.

Voids– While the swelling value for the 28 dpa material agrees well with the measurement by Huang [26] the measured swelling value for the 0.4 dpa material is slightly lower than measured by Huang (0.13% vs. 0.23%). The difference is most likely due to the observed local swelling variability at such low dose levels [26]. The presence of more than expected voids in these low dose rate material compared to that of the high dose rate material once again demonstrates the now well-established acceleration of swelling with decreasing dose rate in austenitic stainless steels [2, 3, 13, 14, 43-51].

Second phase precipitation – There is extensive literature on the formation of second phase precipitates (Ni_3Si , phosphides, G-phase, carbides) in irradiated stainless steels [52-57]. In particular, γ' (Ni_3Si) precipitates and G phase have been shown to be stable only in the presence of irradiation [58-61]. The γ' phase has been found to dominate at relatively low ($\leq 450^\circ\text{C}$)

irradiation temperatures, although it has been shown that the temperature regime of γ' can shift with changes in dpa rate [62].

While there is relatively good agreement between this work and that of Huang where comparisons can be made, the current study provides a much richer understanding than can be provided with conventional TEM on a larger specimen, especially when energy dispersive spectroscopy measurements cannot be reliably made due to high radioactivation of the specimen.

The Ni and Si-rich precipitates observed in the present study are consistent with the early stages of formation of γ' phase. In the 0.4 dpa material, the Ni/Si precipitates exhibit a core-shell structure with a Ni-to-Si ratio of 4.0 ± 0.8 at the core, and an even higher ratio in the shell, deviating from the expected stoichiometry of the γ' phase (Ni_3Si). Considering the low dose received by the 0.4 dpa material, it is thought to be likely that the precipitates observed are precursors to γ' or G phase, surrounded by Ni and Si segregation induced by irradiation. In the 28 dpa material, the Ni/Si precipitates no longer show the core shell structure and the Ni-to-Si ratio is 3.0 ± 0.2 at the peak position in the profile (**Figure 3**), which is consistent with the stoichiometry of $\text{Ni}_3\text{Si } \gamma'$. The presence of Nb inside the precipitates in both of the low dose and high dose material suggests that the precipitate may have nucleated on Nb clusters acting as defect sinks. In addition, previous observations have shown that Nb can substitute for Si in γ' [58]. The nucleation of γ' on dislocations in the 28 dpa material also suggests a strong role of defect sinks in the precipitation process. Renault [8] and Toyama [63] reported the presence of γ' in irradiated 304SS, but these studies involved different temperatures, dpa rates, and differences in minor elemental compositions, so the exact conditions for γ' formation in any given case cannot be firmly established at this time with the limited data available.

The G phase was also found in the 28 dpa condition. G phase has previously been reported to exhibit a small rod shape [38], matching with the APT observation in this study. Formation of G phase has been observed in neutron-irradiated 316 SS at temperatures ranging between 460 to 650 °C [57], probably more easily as a consequence of the higher nickel level in 316SS.

In addition to Ni/Si precipitates, pairs of P-rich plates were observed by APT. Prior observations have reported the presence of M_2P type phosphide rods with their axis parallel to the $\langle 100 \rangle$ direction [64-67]. However, the P-rich plates observed in this work are on (111) planes. The

similarities in size and orientation suggest that the phosphide plates observed by APT might be related to the defects imaged by TEM as seen in **Figure 5** and in Huang's work [26] where these were identified as (111) stacking faults within Frank loops. While segregation to dislocation loops to form γ' has often been observed, these loops might also act as nucleation sites for the phosphide plates revealed by APT.

Grain boundary precipitates – Carbide precipitates were observed on grain boundaries in both low dose and high dose conditions. Irrespective of size and conditions, the measured C-to-Cr ratio and electron diffraction analysis are consistent with the $M_{23}C_6$ phase. Toyama also studied grain boundary chemistry in neutron-irradiated 304SS at 300°C, but reported no precipitates [68]. The formation of carbides is likely the result of an interplay between an irradiation temperature close to the sensitization temperature range of 304, typically 450° C to 800 °C, and irradiation accelerated diffusion, leading to larger carbides in the 28 dpa material. Nano-sized Fe and Ni clusters observed inside of the carbide phase suggest that carbides are also subject to irradiation damage and irradiation-induced clustering. In addition to carbides, carbon-silicides were also observed on grain boundaries in the high dose material. The carbon-silicides observed in this study might be the same Ni, Si and Cr rich precipitates previously reported at grain boundaries of 304 SS irradiated in EBR-II to 10-12 dpa at $<5.10^{-8}$ dpa/s [69-71].

Solute segregation to dislocations, interfaces, and grain boundaries – Solutes such as Mo, B, C, P and S are segregated to grain boundaries prior to irradiation, in agreement with Tomozawa et al. [72]. Slight Cr segregation is also observed, in agreement with previous APT analysis on the same material before irradiation [73]. Cr segregation can be attributed to the combination of a thermodynamic driving force leading to small segregation behavior [74] and non-equilibrium segregation from the loss at grain boundaries of the supersaturation of vacancies developing during the cooling process [75]. Alternatively in 0.4 dpa material, an overall depletion of Cr with or without local segregation at the grain boundary (or the W-shape profile). This Cr depletion is always associated with Ni, P, and C enrichment. We also note that the regions of grain boundaries next to carbide and phosphide particles have different segregation behaviors. Both a sensitization mechanism (i.e. the formation and growth of carbide and phosphide particles) and radiation-induced segregation by an inverse Kirkendall mechanism [76, 77] can explain the observed grain boundary chemistry. As observed by Allen et al. [69-71, 78], grain boundary

precipitation can significantly alter grain boundary composition and the associated radiation-induced segregation profiles. Comparable Cr depletion at grain boundaries has been reported in numerous studies of irradiated steels, e.g. [68, 76, 78-82].

The observed segregation of Ni and Si, to grain boundaries and dislocations agrees with prior literature [68, 76, 78-82], and has been explained by an inverse Kirkendall effect [77]. The segregation of smaller solute atoms such as Si and P has been explained in terms of a solute drag effect, leading to a non-equilibrium accumulation of these elements at defect sinks [76]. The segregation of these elements to the carbide and phosphide interfaces (**Figure 9**) and dislocations (**Figure 5**) also agrees with this proposed coupling mechanism.

4. Conclusions

The examination of highly radioactive specimens using conventional electron microscopy on relatively large specimens places some limits on our ability to investigate on the small microstructure level the coupled evolution of defect microstructure and the associated microchemical environment at the various defects. In this study, we have conducted APT analysis on very small specimens, reproducing not only the microstructural results obtained by conventional microscopy on identical material, but also adding significant insight concerning the coevolution of microstructure and microchemistry, especially that associated with strong sinks such as dislocation loops and grain boundaries. There are limitations to small specimen analysis, however, associated with the limited sample volume yielding measureable differences from microscopy sampling of larger volumes. By comparing a very low dose specimen with a much higher dose specimen, both derived from a single irradiated assembly, it has been demonstrated that the coupled evolution of dislocations and other sinks begins very early, with segregation producing what appears to be measurable precursors to fully formed precipitates found at higher doses.

Our major findings are summarized as follow:

- Voids examined in these low dose rate materials yield a higher swelling value than might be expected from extrapolation from high dose rate materials, demonstrating the previously reported acceleration of swelling with decreasing dose rate in austenitic stainless steels.

- If the voids are relatively small compared to the dimensions of the FIB specimen and the void distribution is not too heterogeneous, good swelling agreement can be attained between large and small specimen techniques.
- Aggregations that appear to be precursors to Ni_3Si precipitates formed on Nb clusters are found in the low dose condition while fully formed Ni_3Si precipitates are observed in the high dose condition, especially on strong sinks like dislocation loops, indicating that the coupled evolution of microstructure and microchemistry starts at very low dose levels.
- All defects sinks (dislocations, Ni_3Si clusters, phosphide interfaces, carbide interfaces, grain boundaries) are found segregated with Ni and Si in both low and high dose conditions.
- While quantifying dislocation loop density and size, as well as the nature of the dislocation loop, from the small APT volume is a challenge, the presence of such structures is clearly revealed with Ni, Si and P segregation to dislocation lines.
- At low dose, even though small carbides are observed, the grain boundary chemistry appears to be controlled by a radiation induced depletion of Cr and segregation of Ni and Si. However, high angle grain boundaries are continuously decorated by carbide precipitates in the high dose condition.

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Table 1 Chemical composition of 304SS as measured by ICP-AES [27] and matrix composition as measured by APT over 39 million ions. Errors of APT measurements were calculated from dataset to dataset variations and counting statistics within each dataset.

	Cr	Ni	Mn	Co	V	Mo	Cu	Si	C	P	S
ICP (wt.%)	19.26	8.81	1.57	-	-	-	-	0.43	0.06	0.03	0.03
ICP (at.%)	20.34	8.24	1.57	-	-	-	-	0.84	0.26	0.05	0.05
APT (at.%)	19.9	8.0	1.57	0.18	0.04	0.11	0.18	0.81	0.23	0.03	0.007
(as received)	±0.3	±0.2	±0.02	±0.03	±0.01	±0.05	±0.01	±0.05	±0.03	±0.01	±0.005
APT (at.%)	18.7	7.8	1.40	0.12	0.04	0.05	0.19	1.01	0.17	0.01	0.002
(low dose)	±0.9	±0.5	±0.13	±0.04	±0.01	±0.02	±0.07	±0.20	±0.05	±0.01	±0.001
APT (at.%)	19.5	7.6	1.56	0.12	0.05	0.05	0.09	0.89	0.12	0.01	0.005
(high dose)	±0.4	±0.5	±0.13	±0.02	±0.01	±0.02	±0.03	±0.20	±0.06	±0.01	±0.005

Table 2 Gibbsian interfacial excess (nm^{-2}) of segregating solutes in unirradiated 304SS.

Cr	B	C	P	Mo	S
1.80 ± 0.30	1.20 ± 0.07	1.04 ± 0.06	0.45 ± 0.05	0.21 ± 0.07	0.05 ± 0.01

Table 3 Gibbsian interfacial excess (nm^{-2}) of segregating solutes calculated from grain boundaries in neutron-irradiated 304SS.

	Ni	Si	Co	Mo	V	B	C	P
15 nm away from phosphides	16.1	2.1	NA	NA	NA	0.19	NA	0.42
>20 nm away from precipitates	18.7±0.7	5.7±1.2	0.38±0.04	0.05±0.02	0.08±0.03	0.15±0.02	0.63±0.38	1.04±0.20

Table 4 Composition (at.%) measured from clusters inside carbide A and carbide matrix.

	Fe	Cr	Ni	Mn	V	Co	Mo	Cu	C	Si	P	B
Clusters	48.8	30.0	10.9	0.64	0.05	0.06	0.04	0.03	9.1	0.32	0.07	0.08
	±5.3	±1.4	±2.5	±0.12	±0.02	±0.01	±0.01	±0.01	±1.1	±0.18	±0.01	±0.03
Matrix	15.5	64.5	1.57	0.64	0.12	0.03	0.09	0.01	16.9	0.16	0.08	0.13
	±1.4	±0.4	±0.04	±0.12	±0.02	±0.01	±0.01	±0.01	±0.8	±0.08	±0.02	±0.04

Figure 1: (a) maps from the unirradiated archive material showing uniform elemental distributions in the matrix; (b) maps containing a high angle grain boundary; (c) Fe, Cr and Ni concentration profiles measured along a 10 nm diameter cylinder across the grain boundary shown in (b).

Figure 2 TEM images showing voids in (a) 0.4 dpa and (b) 28 dpa materials with the void size distributions (c, d) obtained from 277 and 423 voids respectively.

Figure 3 Reconstructions showing Ni and Si rich precipitates in (a) 0.4 dpa material and (b) 28 dpa material; (c)-(f): line profiles measured by placing a 10 nm diameter cylinder along the arrows indicated in (a) and (b).

Figure 4 (a) APT atomic maps of P-rich precipitates in 0.4 dpa material; (b) line profile measured by placing a 10 nm diameter cylinder along the arrow indicated in (a); (d) TEM image showing the two sets of stacking faults on (111) planes .

Figure 5 (a) APT atomic maps of P-rich precipitates in 28 dpa material; (b) line profile measured by placing a 10 nm diameter cylinder along the arrow indicated in (a).

Figure 6 (a) Reconstructions and maps from the 28 dpa material; (b) line profile measured by placing a 10 nm diameter cylinder along the arrow indicated in (a).

Figure 7 (a) APT atomic maps of one carbide observed in 28 dpa material; (b) line profile measured by placing a 10 nm diameter cylinder along the arrow indicated in (a).

Figure 8 (a) APT atomic maps of ferrite and precipitates next to the ferrite in 28 dpa material; Line profiles measured by placing a 10 nm diameter cylinder along the dashed arrow (b) and solid arrow (c) indicated in (a).

Figure 9 APT atomic maps of dislocation loops in (a) 0.4 dpa material and (b) 28 dpa materials.

Figure 10 (a) Atomic maps of a representative APT dataset that has a high angle grain boundary; (b) line profile measured by placing a 10 nm diameter cylinder along the arrow indicated in (a); (c)-(d) atomic maps showing the presence of (c) carbide and (d) phosphide on grain boundary.

Figure 11: 28 dpa condition: (a) TEM image of precipitates on a randomly chosen high angle grain boundary; (b) EDS line profiles across the blue line in (a), carbon level was not counted as EDS could not accurately detect carbon; (c) EDS line profiles across the red line in (a); (d) electron diffraction patterns taken from four different zone axis of precipitates in (a); (e) atomic maps from APT dataset that contains both carbide and carbon-silicide; (f) line profile measured by placing a 10 nm diameter cylinder across the arrow indicated by the arrow in (e).

Figure 12: 28 dpa condition: (a) TEM image and electron diffraction pattern of ferrite grain on a random high angle grain boundary; (b) EDS line profiles across the red line in (a).