Structural and Chemical Evolution in Neutron Irradiated and Helium-Injected Ferritic ODS PM2000 Alloy

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Abstract

An investigation of the influence of helium on damage evolution under neutron irradiation of an 11 at% Al, 19 at% Cr ODS ferritic PM2000 alloy was carried out in the High Flux Isotope Reactor (HFIR) using a novel *in situ* helium injection (ISHI) technique. Helium was injected into adjacent TEM discs from thermal neutron $^{58}\text{Ni}(n_{\text{th}},\gamma)^{59}\text{Ni}(n_{\text{th}},\alpha)$ reactions in a thin NiAl layer. The PM2000 undergoes concurrent displacement damage from the high-energy neutrons. The ISHI technique allows direct comparisons of regions with and without high concentrations of helium since only the side coated with the NiAl experiences helium injection. The corresponding microstructural and microchemical evolutions were characterized using both conventional and scanning transmission electron microscopy techniques. The evolutions observed include formation of dislocation loops and associated helium bubbles, precipitation of a variety of phases, amorphization of the Al_2YO_3 oxides (which also variously contained internal voids), and several manifestations of solute segregation. Notably, high concentrations of helium had a significant effect on many of these diverse phenomena. These results on PM2000 are compared and contrasted to the evolution of so-called nanostructured ferritic alloys (NFA).

1. Introduction

Irradiation of structural materials with energetic neutrons at elevated temperatures results in structural and chemical changes beginning at the nanoscale that degrade their performance sustaining properties [1-4]. Prediction of material performance in intense irradiation environments, such as those experienced by a fusion first wall or in fission reactor core components, requires an understanding of events that occur over an enormous range of spatial and temporal scales. This poses a significant materials challenge, both from the perspective of conducting meaningful experiments in suitable timeframes, as well as developing predictive models. Neutron-induced displacement damage produces isolated self-interstitials, vacancies and clusters of these defects that interact to yield an evolving microstructure, and in many cases leads to substantial material degradation over the operating service lifetime. Key challenges that can arise due to the structural and chemical changes that occur under neutron irradiation include loss of ductility and fracture toughness, large increases in yield strength, dimensional instabilities due to swelling and irradiation creep, changes in deformation behavior as well as thermal and electrical conductivity. However, unlike the fission environment, a fusion first wall suffers from high-energy neutron n,α reactions that generate large concentrations of helium at rates of 10 appm He/dpa, where dpa is displacements per atom.

Target end-of-life dpa levels correspond to thousands of appm of helium. Helium is an undesirable gaseous transmutant atom that first precipitates as pressurized, nanometer sized gas bubbles that initially grow only with the addition of helium. Yet, upon reaching a critical size of approximately 3 nm, the bubbles can transition into faceted voids that grow unstably via a bias driven flux of excess vacancies without the need for additional helium [1,5-8]. While the helium bubbles can themselves lead to substantial degradation of the mechanical properties, the transition to voids and resulting void swelling can lead to dimensional changes that further compromise structural integrity. To address these issues, microstructural design of new iron-based alloys is being pursued to control the large helium inventory. The ultimate goal is twofold, 1) limit the ability of helium to form bubbles that can reach the critical size for unstable void growth, and 2) minimize the diffusion of helium to grain boundaries where it can eventually lead to various manifestations of embrittlement.

Oxide-dispersion-strengthened (ODS) ferritic alloys have emerged as an attractive class of structural materials for both advanced nuclear fission and fusion applications. In particular, the nanostructured ferritic alloy (NFA) variants manifest a combination of high tensile, creep, and fatigue strengths, coupled with a high resistance to the effects of irradiation [4,6,7]. This is achieved because the NFAs contain an ultrahigh number density ($>10^{23}/\text{m}^3$) of 1-5 nm Y-Ti-O oxides, have fine grain sizes on the order of 1-2 μm , and a high dislocation density.

PM2000 is a different ODS ferritic alloy that contains a higher Cr concentration compared to NFA, and has Al added to improve its corrosion resistance. This mechanically alloyed FeCrAl alloy also has ~ 0.2 wt% Y_2O_3 , but during thermomechanical processing this oxide phase is converted to yield a much different distribution of ODS particles than found in NFAs. Mechanical alloying of the starting powders and hot consolidation leads to a dispersion of Y-Al-O oxide precipitates with an average diameter of 20-30 nm at a density of $\sim 10^{21} \text{ m}^{-3}$, considerably more coarse than

NFA. This coarser distribution of oxide particles is less effective in stabilizing both small grain sizes and high dislocation densities and gives overall lower strength as compared to NFAs. The advantage of PM2000 is that the Al addition imparts better corrosion and oxidation resistance due to a durable passivating Al_2O_3 surface scale, which supports its consideration for applications such as lead-bismuth eutectic cooled advanced fission reactors and as accident tolerant fuel cladding for commercial light water reactors [12-14]. The relative irradiation tolerance of this latter class of ODS ferritic stainless steels has yet to be systematically explored, especially in the presence of high levels of helium. While the Al content precludes PM2000 from being considered as a reduced activation alloy and thus as a candidate for fusion first wall applications, the different grain structure and ODS distribution does provide a useful basis for comparison of dpa and He effects in the NFAs versus ODS steels.

Limited studies of the microstructural response of PM2000 to self-ion and α particle irradiation have been reported [15-22], but there is little to no data on neutron-irradiation effects. Fields et al [23] and Edmondson et al [24] reported on the microstructural response of four FeCrAl alloys irradiated with neutrons at 593K, but these were not ODS alloys. The self-ion and α -particle irradiations suggest that the Y-Al-O precipitates are very stable under charged particle irradiation, but can trap helium that leads to bubble and void formation on matrix/particle interfaces. One of these studies also found evidence of a strong association between helium bubbles and dislocation loops that formed when PM2000 was implanted with α particles under uniaxial stress [20].

To properly study the response of PM2000 under fusion first wall conditions requires specially designed neutron irradiation experiments. An *in situ* helium injection (ISHI) technique [25-28] was used to produce simultaneous helium and displacement (dpa) damage in PM2000 in mixed fast-thermal spectrum irradiations in the High Flux Isotope Reactor. We present the first results obtained for PM2000 that explore the microchemical and microstructural changes that occur both with and without concurrent helium injection.

2. Experimental

The PM2000 alloy irradiated and characterized in this study is a commercial Plansee GmbH product with a very coarse grain size of ~ 1 mm. The approximate alloy composition (at%) is 69% Fe, 19% Cr, 11% Al, 0.5% Ti, 0.2% Y_2O_3 , 0.1~0.2% C. This was determined by energy dispersive spectroscopy (EDS) from a large area of a representative sample using an FEI Quanta 3D scanning electron microscope equipped with an Oxford Instruments INCA EDS system.

An irradiation experiment was designed to achieve high He/dpa ratios in a fission reactor by taking advantage of the two-step $^{58}\text{Ni}(n_{\text{th}},\gamma)^{59}\text{Ni}(n_{\text{th}},\alpha)$ reaction, which ejects a 4.79 MeV alpha particle [26-28]. In order to avoid changing the actual alloy chemistry via direct Ni doping, a thin NiAl film was deposited on the surface of a disc of PM2000. When irradiated in a mixed spectrum reactor, a fraction of the 4.76 MeV alpha particles are injected into the ferritic substrate over a uniform depth of up to $\sim 6 - 9$ μm . The depth of uniform helium injection is a function of the thickness of the film, which also controls the helium and He/dpa ratio. In this experiment, 3mm discs, with an approximate thickness of ~ 250 μm , were coated on one side with a 4 μm thick NiAl film that injects helium into adjacent discs on both sides of the film (one coated and the other uncoated).

This provides two irradiation conditions in the same sample: a helium-injected region adjacent to the NiAl coating with concurrent neutron damage and the remainder of the disc that experiences only neutron irradiation. For brevity, the two sides of the disc will be referred to as the ISHI side and the neutron irradiated only (NIO) side. The discs were irradiated over several cycles in the High Flux Isotope Reactor at 773K to ~21 dpa. Approximately 1230 appm of helium were uniformly injected into the PM2000 disks [26-28]. An unirradiated PM2000 control condition was also examined.

Transmission electron microscopy (TEM) cross-section specimens were prepared by focused-ion-beam (FIB) milling using an FEI Quanta 3D FIB. Each TEM lamella was given a final 2 kV thinning and further cleaned by low energy (600 eV) Ar for 10~15 min at 8° incident angle using a Fischione NanoMill® 1040 to remove amorphization at the surface caused by the FIB milling process.. The FIB lamella extracted from the ISHI side of the disc spanned a minimum depth of 6 μm from the NiAl film, thus sampling the entire region of uniform helium implantation. To obtain TEM samples that experienced only neutron irradiation, FIB lamellae were extracted from the opposite side of the same disc. Each FIB lamella was extracted by milling directly through the outer surface of the disc; for the ISHI side the FIB lamellae included the 4 μm NiAl coating. TEM examination revealed that some diffusion of Ni occurred into the PM2000 alloy substrate to a depth between 500 to 1000 nm. All examinations were performed 2 - 3 microns past this region. Owing to the very large grain size of this heat of PM2000, no grain boundaries were observed in any of the FIB lamellae.

General microstructural characterization was performed using both a JEOL 2010F Field Emission Gun (FEG) TEM and an FEI Tecnai F20 FEG TEM. Dislocation analysis was performed using 2-beam bright field (2B-BF) imaging conditions, typically with g 002-type reflections obtained by tilting 6 to 8° off the matrix [001] zone axis. Analysis of the dislocation structures followed the method proposed by Yao et al. [29] for similar neutron-irradiated ferritic steels. Nanodiffraction and selected area diffraction were used to identify the various phases and structures of interest. Drift corrected elemental mapping using an Oxford Instruments INCA EDS system on the JEOL 2010F was performed using approximate probe sizes of 0.7 to 1 nm for ~2 - 3 h, which provided an effective exposure time for each pixel of more than 20 s. Energy filtered TEM (EFTEM) was performed using spectra at 580~600 and 710~730 eV for the Cr $L_{2,3}$ and Fe $L_{2,3}$ edges, respectively. The 3-window method for background subtraction was performed using a Gatan image filter with exposure times between 10-20 s and a GIF entrance aperture of 2.5 mm.

3. Results

ATEM characterization of the irradiated alloy revealed several surprising and notable effects of both irradiation and ISHI. First, significant changes occurred in the chemistry, crystal structure and morphology of the oxide precipitates. Secondly, irradiated PM2000 developed dislocation and cavity structures that appear to be unique among irradiated ODS and NFA alloys. Finally, extensive radiation-induced precipitation occurred throughout the matrix, as well as radiation-induced segregation to various sinks within the grain interiors. Each observation will be discussed below.

3.1. Characterization of the Oxide Particles

The oxide particles in the unirradiated sample were examined thoroughly to probe their size, density, crystal structure and chemistry. The oxides were often faceted and randomly dispersed throughout the grain interior at a density of $\sim 10^{21} \text{ m}^{-3}$. In order to deduce the crystal structure of the oxide precipitates, their chemistry was measured using EDS elemental mapping (see Figure 1), and then combined with information extracted from the FFT of the lattice image (Figure 2b). Based on the chemistry and plane spacing and angle information, CrystalMaker was used to explore various combinations of crystal structures to explain the results. A summary of the particle statistics and particle chemistry is presented in Tables 1 and 2, for unirradiated PM2000 and both irradiation conditions (the latter to be discussed later). Oxygen was not included in the quantitative analysis of the particles because it cannot be accurately measured in such thin foils, especially when Cr is present due to peak overlap. In this analysis of the ODS particles the Fe and Cr were left out of the quantitative analysis because the maps indicated each element was depleted in these particles. Based on the fact that the oxides in the unirradiated condition possess a Y/Al ratio of 0.96, they appeared to be YAlO_3 , which has been reported by Klimiankou [11].

A HRTEM image taken of an octagonal shaped oxide particle (yellow-dotted line outlines the boundary) in the unirradiated sample is shown in Figure 2a, along with an FFT from the same particle in Figure 2b. This particle is approximately 30 nm wide, and hence is not through thickness of the TEM sample. Therefore, lattice reflections of the Fe matrix are observed in the FFT. A close examination of the HRTEM lattice image, shown in Figure 2c, reveals that the right angle relationship of the two planes with interplanar spacing of 2.10 Å and 2.63 Å can only be satisfied by the (022) and (-121) planes on [311] zone of YAlO_3 (Yttrium Aluminum Perovskite or YAP, Orthorhombic, Pnma, $a = 5.33 \text{ Å}$, $b = 7.37 \text{ Å}$, $c = 5.18 \text{ Å}$) [29]. This was subsequently confirmed by matching the FFT in Figure 2b with the unit cell and [311] zone projection view of YAlO_3 in Figure 2e. The orientation relationship between the matrix and precipitate was determined to be $\langle 001 \rangle_{\text{m}} // \langle 311 \rangle_{\text{p}}$, $\perp \{110\}_{\text{m}} // \perp \{022\}_{\text{p}}$ and $\perp \{110\}_{\text{m}} // \perp \{121\}_{\text{p}}$.

As shown in Figure 3, neutron irradiation had a profound effect on the oxide precipitates, leading to complete amorphization accompanied by transformation to a more rounded morphology. As shown in Table 1, compared to the unirradiated condition the loss of crystallinity and change in morphology did not yield significant differences with respect to the oxide mean size or size distribution as shown in Figure 4. Table 2 does show that the amorphous particles in the NIO side have an increased Y/Al ratio of 1.44, whereas in the ISHI side the particles have a Y/Al of ~ 1 , similar to the unirradiated, crystalline particles. Figure 5 presents examples of the amorphous oxides in both the NIO and ISHI sides with accompanying diffraction measurements that confirm their amorphous structure. The diffraction patterns have diffuse rings/halos produced by the amorphous ODS particles. By selecting any portion of the halo with the objective aperture in the TEM, all amorphous oxide particles will be visible in dark field. The number densities are similar for the unirradiated and ISHI conditions but are nominally lower for the NIO condition (see Table 1). However, this discrepancy is most likely due to poor statistics since the particle distributions were taken from FIB lamellae, and not larger electropolished TEM discs that allow better sampling of the oxides particles.

In addition to the amorphization, 100% of the oxides in the ISHI side contained a single, large void, compared to 22% of the oxides in the NIO region (Figure 3). These voids ranged in size from 3 to 20 nm in diameter. In each case, the voids were completely enveloped within the boundary of the associated oxide particle, indicating the voids form inside the particle, not located at the oxide/matrix interface. It is interesting that voids still form inside some of the oxide particles even in the absence of high levels of injected helium. A plot of the void size versus the associated oxide particle size is shown in Figure 5. There is a cluster of void/oxide particle sizes in the ISHI side at a ratio of $\approx 1/3$. The data are more scattered in the NIO side, perhaps due to the lower overall fraction of oxides containing voids. The reason that spherical amorphous oxides form internal voids, while faceted crystalline oxides in NFAs form interface bubbles is not understood. The fact that helium injection promotes internal void formation in the oxide particles means that helium must dissolve in the particles, consistent with first principles calculations on a variety of other oxides [30,31]. As noted earlier, the Y/Al ratio between the ODS particles in the NIO versus ISHI side of the foil differs considerably, but the relationship to the amorphization and difference in internal voids is unclear.

3.2. Dislocation Microstructure

TEM micrographs of typical dislocation structures in PM2000 are shown in Figures 6 and 7, with the corresponding relevant statistics summarized in Table 3 for the three different conditions. Unirradiated PM2000 mostly contains small dislocation line segments at a relatively low density of $\sim 10^{14}/\text{m}^2$. Irradiation with neutrons only produces a slightly higher density of line segments ($2.2 \times 10^{14}/\text{m}^2$), mainly aligned along $\langle 100 \rangle$ directions, and a low density of small dislocation loops of both $\langle 100 \rangle\{100\}$ and $\frac{1}{2}\langle 111 \rangle\{111\}$ character. In contrast, ISHI produced a much higher density of larger dislocation loops of both types. The $\langle 100 \rangle$ type loops are present in significantly higher densities than the $\frac{1}{2}\langle 111 \rangle$ loops in the NIO region, and this difference is further increased in the ISHI region. The $\langle 100 \rangle$ loop diameters extend up to ~ 150 nm. The dislocation structure is highly organized into generally well-separated loops, but with some evidence that dislocation tangles are beginning to form in the ISHI region.

As shown in Figure 7, each dislocation loop in the ISHI side is associated with multiple small helium bubbles, similar to what was reported by Chen et al [20] in dual Fe/ α ion irradiations of irradiation of PM2000. Approximately 90% of the bubbles are associated with visible dislocation loops. The measured size distributions for helium bubbles and the low density of voids observed in the ISHI region are compared in Figure 8. The bubbles attached to the loops are present in a narrow size range, rarely exceeding 2 nm in diameter and averaging 1.4 nm. A much lower density of helium bubbles ($< 10^{21}$ per m^3) exists in the NIO side of the foil. These bubbles may be the result of helium produced by transmutation of base metal and residual boron impurities. We estimate that up to 10 appm of helium could be produced at this dose just from transmutation of the base metal alone. This low level of helium may be the source of the voids that were observed in the oxides in the NIO side, but why only some particles contain voids remains unclear. The bubbles in the NIO side of the foil are also attached to both types of loops. A small fraction of bubbles do not appear to be associated with visible dislocation loops but this may be due to loops with Burgers vectors that are not in contrast for the imaging conditions used. There also appear to be a low density of helium

bubbles associated with the large oxides, but these may be projected images of bubbles in the matrix above and below the oxide particle. As noted previously, the loop structure is not as well developed in the NIO side compared to the ISHI region, and the ratio of $\langle 100 \rangle$ to $\langle 111 \rangle$ -type loops is lower. No grain boundaries or interfaces, other than the oxides as described below, were observed due to the large grain size.

3.3. Radiation-Induced Chemical Changes

Figure 9 shows examples of STEM-EDS mapping of the irradiation-induced segregation and precipitation observed in PM2000. STEM-EDS analysis reveals various chemical changes that develop under neutron irradiation. Some changes are associated with the dislocation loops and oxides, while others appear to be independent of these features. The STEM/EDS mapping results show a mixture of isolated Cr-rich regions and a percolated structure of Cr-enrichment extending from the amorphous YAlO_3 precipitates. These Cr-rich features are similar in the NIO and ISHI sides of the foil. The STEM/EDS mapping shown in Figure 9 also reveals that the amorphous YAlO_3 particles, which have the same Y/Al ratio after irradiation (Table 2), have a Cr-rich shell (Cr-segregated/Fe-depleted) at their periphery, similar to that reported by Lozano-Perez [32] and de Castro [33] in two Fe-Cr- Y_2O_3 model ODS alloys. Both elemental mapping with EDS and energy-filtered TEM mapping also demonstrated (see Figure 10) that Cr is highly enriched at the periphery of the dislocation loops, along with corresponding Fe depletion.

The elemental mapping clearly shows that Al and Ti co-segregate in both regions of the foil, forming a second phase that is distinct and discrete from the Cr-rich features (Figure 9). However, the matrix Ti is less depleted in the ISHI region. To confirm the EDS results of second phase precipitation, compelling evidence was found when examining selected area diffraction (SAD) patterns. The SAD patterns in Figure 11 show only body centered cubic (bcc) reflections for the unirradiated sample, whereas for the irradiated samples the SAD patterns reveal extra reflections from radiation-induced precipitates that form in both the ISHI and NIO sides of the foil. Analysis of the extra reflections indicates these precipitates possess a face centered cubic (fcc) structure, with a cube-on-cube orientation relationship with the ferrite matrix, and a lattice parameter that is exactly 2x larger than bcc Fe. A simulated pattern showing the orientation relationship between the two phases is shown in Figure 11c. Further evidence that both sides of the disc contain fcc precipitates is seen in the BFTEM/DFTEM images in Figure 12. Using dark field imaging from the discrete precipitate reflections, small, irregularly shaped fcc precipitates clustered in a seemingly interconnected network were observed in both regions of the foil. It should be noted that amorphous YAlO_3 oxide precipitates are also visible in the DFTEM images because the diffuse ring/halo from the amorphous YAlO_3 oxide is captured along with the fcc precipitate reflection. The agglomerated fcc precipitates tend to form in regions away from the oxides, implying that the Cr-rich shell (high Cr/low Al/low Ti) adjacent to the oxides hinders the formation of these second phase precipitates.

Based on precipitate diffraction patterns obtained in this study (see Fig. 12b), and comparison to previous work [34-37], the measured lattice parameter is 5.74 Å (which is 2 times larger than for bcc Fe and 0.9% smaller than for pure Fe_3Al). This small difference is likely due to compositional differences resulting from substituting other elements for Fe and Al. Figure 13 shows a direct comparison between eight pure bcc Fe

unit cells, a Fe₃Al (fcc) unit cell, and a Cr, Ti alloyed Fe₃Al (fcc) unit cell to help visualize the site occupancies of the respective elements in the proposed (Fe_{0.55}Cr_{0.2}Ti_{0.05})Al_{0.2} phase. This composition is consistent with Al atoms ordering at face centers and corners of a super cell composed of eight Fe (bcc) unit cells, corresponding to Fe₃Al (see Figure 13b).

Additional evidence for the proposed fcc phase and associated substitution of Cr and Ti is provided by results of *ab initio* calculations that investigated whether 3d transition metal impurities can occupy the two different Fe sites in the Fe₃Al (D03) structure, which are the Fe_I (8 Fe neighbors) and Fe_{II} sites (4 Fe and 4 Al neighbors) shown in Figure 13 [37]. These calculations showed that Cr and Ti can preferentially substitute in the Fe_I site (orange) causing a decrease and increase in the lattice constant, respectively. Thus, the higher levels of Cr versus Ti (20 at% versus 5 at%, respectively) are expected to decrease the lattice constant of Fe₃Al, and to provide some degree of coherency with the α Fe matrix as indicated in the diffraction analyses presented in Figure 13. Specifically, Ti segregates to the fcc phase, while Cr is only marginally higher than in the matrix. However, our results indicate that some Al sites may also be occupied by Cr and Ti in the sense that the Fe:Al ratio of (Fe_{0.55}Cr_{0.2}Ti_{0.05})Al_{0.2} is 80:20 if Cr and Ti replace only Fe, while that of Fe₃Al is 75:25. In other words, the fcc structure of Fe₃Al is maintained even though one fifth of the Al sites at face-centers and corners are occupied by Cr and Ti.

As a final observation, Capdevila et al [38] reported that a Ti,Al-rich precipitate formed in their aged PM2000, which they assigned to a B2 Fe(Ti,Al) β' phase based on a composition obtained from APT. This composition was 11 at% Cr, 25 at% Al and 15 at% Ti, considerably different than found in this study.

4. Discussion

This study of helium and neutron irradiation effects in PM2000 ODS steel revealed significant differences as compared to NFAs such as 14YWT, 12YWT, and MA957. The NFA nomenclature was proposed by Odette [7] as a class of ferritic stainless steels distinct from the ODS variant. NFAs contain a much finer distribution of nano-features (NFs) with sizes peaked around 2-3 nm at very high number densities of $\sim 5 \times 10^{23}/\text{m}^3$. Like PM2000, the NFAs are mechanically alloyed Fe-based alloys that contain ≥ 12 wt% Cr and small additions of Y, Ti and O. Careful control of processing parameters can yield remarkable microstructural stability at elevated temperatures [39], as well as a very high tolerance for helium [40]. Numerous irradiation studies on these alloys have shown conclusively that the oxide dispersions are stable under neutron irradiation at elevated temperatures to doses of several tens of dpa, with and without helium [7,40,41]. Although PM2000 and NFAs contain similar levels of Ti, the results of this study confirm the work of others [11], that in the presence of ~ 11 at% Al, Ti is not found in the coarser Y-Al-O oxides.

The grain size in the PM2000 alloy studied here is also orders of magnitude larger than in NFAs. Perhaps as a consequence of this large grain size, a very stable microstructure composed of both $\langle 100 \rangle$ and $\frac{1}{2}\langle 111 \rangle$ dislocation loops form in the absence of a high grain boundary sink strength. Dislocation loops are sinks for interstitial and vacancy defects, and trap helium in direct competition with the Y-Al-O precipitates. The $\langle 100 \rangle$ loops are present at higher densities and larger sizes than the $\frac{1}{2}\langle 111 \rangle$ loops, a difference that may have been further enhanced by the presence of helium. The

predominant $\langle 100 \rangle$ loops presumably provide higher sink strength for defects and bias factor for interstitial atoms, and are more effective helium traps, due to a larger Burgers vector and corresponding excess volume. Note, as shown by Klimiankou et al [11], PM2000 can be processed to have comparable grain sizes to NFAs, but this variant was not included in this irradiation experiment.

The observations of Cr precipitation and segregation are broadly consistent with the previous results in the literature [40,42,43]. The 19% Cr in PM2000 falls well within the accepted α - α' two-phase region. Perhaps the most surprising result is the extensive Cr segregation to dislocation loops. Such segregation is observed at lower temperatures in sub-saturated alloys, but there are only a few observations at 773 K where 19% Cr falls just above the phase boundary. Neklyudov and Voyevodin reported enrichment of Cr and Si at dislocation loops in 13Cr-2Mo-NbVB steel irradiated to 48 dpa at 848 K with Cr ions [41]. More recently Bhattacharya et al [44] performed self-ion irradiations of high-purity Fe-Cr alloys at 773 K, finding evidence for Cr enriched zones on the habit plane of dislocation loops in an 11% Cr alloy irradiated to a dose of 45 dpa. Atomistic modeling of Cr interaction with dislocation loops in Fe-Cr binary alloys indicate single Cr atoms are weakly bound to the core of edge dislocation loops, with a maximum binding energy of 0.1 eV. This study also revealed that the interaction between a Cr atom located in a dislocation core and another Cr atom nearby is repulsive, suggesting that Cr segregation to dislocation loops might not be favorable when the bulk Cr concentration is greater than $\sim 10\%$ [45], at variance with the present results. Recent Metropolis Monte Carlo simulations show Cr enrichment near mis-coordinated regions of $\langle 100 \rangle$ and $\langle 111 \rangle$ dislocation loops in an Fe-10%Cr alloy, with enrichment greatest at 300 K and decreasing as the temperature increased, but enrichment was still found up to 900 K [46]. Note, such segregation should not be confused with spinodal decomposition, which requires a much higher level of Cr, at least in terms of thermal aging in this temperature range. For example, Capdevila et al. report spheroidal α' phase separation that led to Cr-rich/Al-poor particles reported in PM2000 after aging for 3600 h at 748K [11], consistent with the very large literature on so-called 748 K thermal embrittlement in high Cr alloys [43]. However, segregation to dislocations was not reported.

The presence of the large populations of dislocation loops in both the ISHI side and NIO side of PM2000 can be partially attributed to the relatively low start-of-life sink strength associated with the large grain size of the material investigated here. This raises a question as to why the observed loop structure evolves, and what impact helium has on this behavior. Enhancement of the loops in the implanted region can be rationalized by the accumulation of vacancies in bubbles. Indeed, the loops in the implanted region are associated with helium bubbles that decorate their habit planes as well as their edges. This has been previously reported in α -irradiated samples [17,45]. Brimbal et al [47] provide perhaps the clearest example of pure Fe irradiated simultaneously with both Fe ions and α -particles, finding that at 1 dpa and 500 appm of helium the $\langle 100 \rangle$ loops dominated the microstructure and were decorated with helium bubbles. Their conclusion is that the loops trap helium at their edges that eventually form small bubbles. The loop-bubble “complex” then grows in a symbiotic fashion, with self-interstitial atoms (SIA) partitioning to the growing loop while vacancies accumulate at bubbles in order to accommodate the helium. Note the classical mechanism of loop [48-51] or SIA [52] punching is unlikely in the vacancy rich environment in the ISHI irradiation, since

bubbles should quickly equilibrate. Chen et al [20,21] proposed that if the bubbles are over pressurized then a counter flow of vacancies and SIAs would occur where the latter plate out on the climbing loop. This situation is analogous to the growth of voids on grain boundaries under stress where SIAs are redistributed from bubble surfaces to nearby dislocation cores. Thus, bubbles continuously form on the loop edges, but are left behind on the habit plane with subsequent loop growth. The strain fields of the loop-bubble complex may shield a habit plane bubble from continued growth by helium accumulation.

The formation of loops with associated helium bubbles is not observed in NFAs. The much finer grain structure reduces the supersaturation of defects and helium is preferentially trapped by the high-density of nanometer-scale oxide particles. Note that, unlike the nanometer-scale oxides in NFAs, neither the α' nor the small fcc precipitates appear to trap helium. However, perhaps most significantly, in the absence of fine-scale oxides, the goal to disperse helium in fine bubbles is to some extent achieved by the large density of dislocation loop-bubble complexes.

The complete amorphization of the YAP particles and associated void formation in some of the particles is an interesting finding. Amorphization of oxide features has been observed previously, but usually for very small $< 1\text{-}2\text{ nm}$ sized nanoclusters. Brandes et al. [53], and Ribis et al. [54,55] found that some of the oxide particles in unirradiated NFAs were amorphous, and did not dissolve under neutron or charged particle irradiation [18]. Other researchers [56-59] have observed amorphization of oxide particles, but the wide range of irradiations conditions and oxide phases investigated do not yield a consistent picture other than the oxide particles do not dissolve under irradiation.

Yang et al, [32] and Jin et al. [33] reported that the Y-Ti-O nano-oxides in the NFAs could potentially act as preferential storage regions for helium, with a capacity that scales with increasing feature volume. Bubbles quickly nucleate and grow at the oxide/matrix interface, where the helium chemical potential is lower than for the interstitial sites in the Y-Ti-O nano-oxides beyond a small size. Chen et al. [21] found large voids and helium bubbles on the oxide/metal interfaces in PM2000 irradiated with α particles at a high He/dpa ratio under uniaxial strain, but not in the oxides particles themselves. Enhancement of cavities in the ISHI region is not unexpected, but the fact that they are also observed in the NIO region indicates that high levels of this transmutation product are not needed for their formation.

5. Conclusions

We report a variety of chemical and microstructural changes in an ODS ferritic PM2000 alloy under simultaneous irradiation by helium and neutrons compared to neutrons only irradiation at 773K:

1. In the ISHI region a high number density of small He bubbles ($< 2\text{ nm}$) form in association with both $< 100 >$ and $\frac{1}{2}< 111 >$ dislocation loops. Helium bubbles decorate all of the dislocation loops.
2. The $< 100 >$ loops are present in a significantly higher numbers and larger size than the $\frac{1}{2}< 111 >$ loops, and this difference is accentuated in the ISHI region.
3. The loops disperse the helium in small bubbles, thereby preventing the formation of matrix voids.

4. Helium and dislocation loops form synergistically as a complex for both types of loops.
5. The YAlO_3 precipitates are completely amorphized in both the ISHI and NIO regions, evolving from a faceted shape to a more spherical morphology.
6. All of the amorphous oxides in the ISHI region contain a single large internal void, whereas in the NIO region only 22% of the particles contain a visible void.
7. A number of chemical changes occur in this material, including:
  - a. Phase separation, which produced a fine distribution of Cr-enriched regions in small spheroidal particles and larger, agglomerated regions that may be related to sinks such as dislocation loops.
  - b. It is not clear if α' is forming in the conventional sense, or if the observed Cr enrichment is just radiation-induced segregation to sinks.
  - c. Cr-enriched shells form around the periphery of Y-Al-O particles.
  - d. Cr,Ti-alloyed Fe_3Al -based fcc precipitates form under irradiation.
  - e. The fcc phase is nominally $(\text{Fe}_{0.55}\text{Cr}_{0.2}\text{Ti}_{0.05})\text{Al}_{0.2}$, exhibiting a cube-on-cube orientation relationship with the Fe matrix with $a_{\text{precipitate}}=2\times a_{\text{Fe}}$
  - f. The fcc precipitates do not form in the Cr-enriched shell around the amorphous Y-Al-O particles, probably due to a lowered Al concentration (< 18 at %).
  - g. Cr segregates to the edges of the dislocation loops while Fe is depleted.
  - h. ISHI results in some Ti segregation to the amorphous YAlO_3 particles.

The results of this study have shown that PM2000 undergoes substantial changes that might significantly degrade its performance. These changes, particularly the chemical segregation and high density of dislocation loops and radiation-induced precipitation, may alter both the corrosion resistance and the mechanical properties of PM2000, especially at higher levels of helium and dpa.

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Figure 1. Elemental maps of the ODS particles and the matrix of unirradiated PM2000.

Figure 2. HRTEM (a) and FFT (b) of a faceted crystalline YAlO_3 particle (outlined in yellow) embedded in the matrix of unirradiated PM2000 oriented on the $[001]_{\text{bcc}}$ zone axis. Close-ups of the lattice images in (c) reveal matched planes of the particle and matrix. The images in (c) were rotated for clarity. The YAlO_3 unit cell is shown in (d) and the $[311]$ zone projection view of YAlO_3 structure is shown in (e).

Figure 3. BFTEM images of the NIO side (a-1) and ISHI side (b-1) after irradiation, showing voids (>2 nm, yellow) formed inside oxide particles. Evidence for oxide particle amorphization is demonstrated by the amorphous ring in the nanobeam diffraction pattern versus SAD from the crystalline matrix (a-2) and a typical amorphous HRTEM image with corresponding FFT (b-2). Statistics of the void and particle distributions are provided in (c).

Figure 4. Box plots comparing the oxide particle size distribution for unirradiated PM2000 with the size distributions for the ISHI and NIO sides of the irradiated foil. Size distribution histograms with 2 nm bin width are shown along with each box plot. The

Figure 5. Comparison of void diameter versus particle diameter for the NIO side on the left and ISHI side on the right. The clustering highlighted in red corresponds to a higher density of particles in this size range.

Figure 7. Three sets of BFTEM images at different magnification with under/in/over-focus near [001] zone from the helium-implanted side: sample is tilted off the [001] zone axis toward the [020] direction to show the presence of helium bubbles on $\langle 100 \rangle \{100\}$ dislocation loops. Note that contrast of helium bubbles are white, none and black respectively at under-focus, in-focus and over-focus.

Figure 8. Box plots, with associated size distributions, comparing the He bubble versus void size distributions measured in the ISHI side of the foil. Note the two distributions use different scales.

Figure 9. STEM-EDS map for Cr, Fe, Y, Al and Ti, and compositional line profile over an oxide particle (on yellow dotted line) from the NIO side (a) and the ISHI side (b). Line profiles extracted from the elemental maps reveal the semi-quantitative chemical concentration of the oxide particles, Cr-shell, and Al-Ti enriched regions. Ti diffuses into oxide particles in the ISHI side while in the NIO side no Ti was found in the particles. Please note the reported concentrations are not absolute, but are averaged through the foil thickness.

Figure 10. Energy-filtered TEM was taken from a dislocation loop in the ISHI side. The top row shows a bright field TEM and energy-filtered TEM images for Cr and Fe, while the bottom row of images show a magnified set of images from the dislocation loop indicated by the orange box visible in the top images. The filtering parameters were (0 ± 10 eV), Cr-related (590 ± 10 eV) and Fe-related (720 ± 10 eV) electrons. Note that the images were taken near a 001 zone axis tilted toward 200 direction (red arrow indicated on BFTEM) by $6 \sim 8^\circ$. The yellow arrows indicate the edge of a $a\langle 100 \rangle$ loop displaying Cr-segregation and corresponding Fe-depletion. Orange box size is $45 \text{ nm} \times 15 \text{ nm}$.

Figure 11. SAD patterns on 011, 001 and 111 zone of (a) unirradiated and (b) ISHI side of the PM2000 samples showing a cube-on-cube oriented fcc phase (green) in the bcc Fe matrix (yellow). The calculated diffraction patterns in (c) show the proposed orientation relationship between the bcc Fe matrix and the Fe₃Al based precipitates. These simulated patterns match the experimental patterns in terms of spacing and positioning.

Figure 12. BFTEM images taken near a 011 zone in (a) the NIO side and (b) the ISHI side. The middle image is an SAD pattern from the corresponding area shown in the BFTEM. Precipitate DFTEM images, shown at the right, were taken using the indicated fcc $g=\bar{1}\bar{1}1$ and fcc $g=\bar{2}00$ respectively. The amorphous oxide particles (indicated by yellow arrows) are also visible because the selected area aperture also captured a portion of the amorphous halo near the fcc diffraction spot.

Figure 13. Unit cell of Cr,Ti-doped (or alloyed) Fe₃Al fcc precipitate with stoichiometry.

Table 1 Mean Oxide Particle Diameters and Number Densities

	Mean Dia. & Std. Deviation (nm)	Density ($\times 10^{20} \text{ m}^{-3}$)
Unirradiated Side	25.8 ± 13.0	12.0
NIO Side	30.0 ± 13.6	4.5

Table 2 Compositions of Oxide Particles and Adjacent Matrix in Unirradiated and Irradiated PM2000 (Oxide composition ignores Fe and Cr)

		at% Cr	at% Fe	at% Al	at% Ti	at% Y	Y/A
Unirradiated	Particle	-----	-----	50.5 ± 3.9	1.0 ± 0.16	48.5 ± 4.0	0.96
	Matrix	18.9 ± 1.9	69.9 ± 1.6	10.6 ± 0.7	0.6 ± 0.5	0.0	
NIO Side	Particle	-----	-----	41.1 ± 4.9	0.85 ± 0.57	59.5 ± 5.0	0.44
	Matrix	19.2 ± 0.1	68.7 ± 0.3	11.4 ± 0.4	0.5 ± 0.0	0.2	
ISHI Side	Particle	-----	-----	50.9 ± 4.4	1.5 ± 0.93	47.7 ± 5.2	0.94
	Matrix	19.4 ± 0.3	69.2 ± 0.6	10.7 ± 0.8	0.6 ± 0.1	0.2	

Table 3 Summary of Microstructural Features: Dislocations and Cavities

	a<100> Loop Density ($10^{20}/\text{m}^3$)	a<100> Loop Size (nm)	$\frac{1}{2}$ a<111> Loop Density ($10^{20}/\text{m}^3$)	$\frac{1}{2}$ a<111> Loop Size (nm)	Line Dislocations ($10^{13}/\text{m}^2$)	Cavity Density ($10^{23}/\text{m}^3$)	Cavity Size (nm)
Unirradiated	N/A	N/A	N/A	N/A	10	N/A	N/A
NIO Side	8.0	17 ± 7.3	4.0	19.6 ± 6.7	22	Helium Bubbles	
						0.01	~1
						Voids	
						0.01	8.8 ± 5.0