A combined APT and SANS investigation of α' phase precipitation in neutron-irradiated model FeCrAl alloys

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Abstract

FeCrAl alloys are currently under consideration for accident-tolerant fuel cladding applications in light water reactors owing to their superior high-temperature oxidation and corrosion resistance compared to the Zr-based alloys currently employed. However, their performance could be limited by precipitation of a Cr-rich α' phase that tends to embrittle high-Cr ferritic Fe-based alloys. In this study, four FeCrAl model alloys with 10–18 at.% Cr and 5.8–9.3 at.% Al were neutron-irradiated to nominal damage doses up to 7.0 displacements per atom at a target temperature of 320°C. Small angle

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neutron scattering techniques were coupled with atom probe tomography to assess the composition and morphology of the resulting α' precipitates. It was demonstrated that Al additions partially destabilize the α' phase, generally resulting in precipitates with lower Cr contents when compared with binary Fe-Cr systems. The precipitate morphology evolution with dose exhibited a transient coarsening regime akin to previously observed behavior in aged Fe-Cr alloys. Similar behavior to predictions of the LSW/UOKV models suggests that α' precipitation in irradiated FeCrAl is a diffusion-limited process with coarsening mechanisms similar to those in thermally aged high-Cr ferritic alloys.

Keywords: Irradiated metals, Precipitation, Atom probe tomography (APT), Neutron diffraction, Ferritic steels

1. Introduction

FeCrAl alloys have shown promise as a new class of alloys for nuclear reactors and power production owing to their excellent high-temperature oxidation and corrosion resistance [1–3]. These alloys are presently under consideration for accident tolerant fuel cladding applications because of their superior performance in steam environments compared with Zr-based alloys, which often exacerbate loss-of-coolant accident conditions as a result of hydrogen gas generation and exothermic oxidation reactions [4, 5]. Current research efforts are focused on developing an optimized candidate FeCrAl alloy that maximizes high-temperature aqueous corrosion and oxidation resistance [6] while maintaining adequate performance with respect to mechanical properties [7–9], processability [7, 10], radiation tolerance [11–15] and neutronics

[16, 17].

Similar to other high-Cr (≥ 9 at.% Cr) ferritic systems, FeCrAl alloys exhibit excellent resistance to radiation-induced swelling [11, 12, 18] but may be prone to hardening and embrittlement partly because of precipitation phenomena occurring at typical light water reactor (LWR) operating temperatures ($<475^\circ\text{C}$) [19]. This phase instability results in the decomposition of body-centered cubic (BCC) high-Cr ferritics into an Fe-rich α matrix phase populated with Cr-rich α' precipitates [19, 20]. This process has been extensively characterized in the Fe-Cr binary system [19–31] and has been shown to form in the FeCrAl ternary system as well [15, 32–37]. Although the kinetics of this precipitation process are normally slow, irradiation is known to accelerate this process by producing freely migrating defects and enhancing diffusion [15, 19, 21, 22].

Al additions are expected to significantly impact the α' precipitation response in this class of alloys, though questions remain regarding how the equilibrium phase distribution and precipitation kinetics are affected. Experimental studies of diffusion multiples by Kobayashi et al. have demonstrated that Al serves to destabilize the α' phase and allows for increased Cr solubility, while recent work by Edmondson et al. has shown that precipitate compositions in FeCrAl alloys are significantly less rich in Cr when compared to binary Fe-Cr systems [15, 21]. Computational work by Bonny et al. has demonstrated that the current thermodynamic models and databases are insufficient for describing the phase transformation behavior in various Fe-Cr alloys [19], which suggests that they are also of limited use for extrapolation of microstructural evolution to the more complex ternary alloy system. As

such, furthering the understanding of the factors affecting α' phase transformation in FeCrAl alloys requires additional systematic experimental study.

This work seeks to expand on and develop this understanding of α' precipitation in FeCrAl and investigate the dose dependencies of this phase instability by examining a single FeCrAl composition neutron-irradiated to three different nominal damage doses under LWR-relevant conditions using atom probe tomography (APT). In addition, an effort is made to correct phase compositions for the effects of neutron absorption/transmutation and trajectory aberration artifacts inherent in the atom probe data. Finally, the same FeCrAl alloys are also investigated using small-angle neutron scattering (SANS) techniques. These two techniques are complementary in that APT provides detailed data on cluster composition and allows for visualization of cluster distribution in a small volume, while SANS yields bulk average precipitate morphology and composition data. Agreement between these techniques helps to overcome the individual limitations of each method and ensures that the resulting quantification is representative of the true microstructure.

2. Materials and Methods

2.1. Specimens and irradiation treatment

Four ferritic FeCrAl model alloys with nominal compositions ranging from 10–18 at.% Cr and 5.8–9.3 at.% Al were fabricated by arc-melting pure element feedstocks of Fe and Cr with pre-alloyed Al-Y specimens. Based on thermodynamic calculations by Capdevila et al. these compositions are all expected to exist within the α - α' miscibility gap but outside of the spinodal

region, such that precipitation is anticipated to proceed by the nucleation and growth mechanism [35, 37]. Yttrium was added as a reactive element to enhance high-temperature oxidation resistance by reducing the growth rate and increasing the adherence of the alumina scale that forms on the surfaces of exposed FeCrAl [38]. These specimens were then hot-forged, rolled, and heat-treated using the conditions developed by Yamamoto et al. [7]. This resulted in a fully ferritic, BCC microstructure with grain sizes on the order of 20–50 μm . Following this heat treatment, the bulk specimens were cold-rolled with a 10% thickness reduction to emulate the cold-shaping process route required for fuel cladding tube production. The composition of these alloys, as determined by inductively coupled plasma optical emission spectroscopy, is shown in Table 1 [14, 15].

The resulting FeCrAl material was cut to form SS-J2 sub-sized tensile specimens using electric discharge machining (the dimensions of which can be found in [14]). These specimens were loaded into capsules for irradiation in the target rod rabbit holder facility of the High Flux Isotope Reactor (HFIR), located at Oak Ridge National Laboratory (ORNL). Individual irradiation target capsules housed six tensile specimens of each of the four FeCrAl compositions. Capsules were irradiated at a target temperature of 320°C at several fluences up to 7.73×10^{21} neutrons/cm², corresponding to nominal damage doses of 0.3, 0.8, 1.8, and 7.0 displacements per atom (dpa). Temperature was measured by performing a dilatometric analysis of passive SiC thermometry bars also contained in the irradiation target capsules [39]. The reported error in irradiation temperature was given by the standard deviation of at least three separate SiC thermometry specimens contained

within the same capsule. A summary of these irradiation conditions can be found in Table 2. Following irradiation, uniaxial tensile tests were performed using shoulder loading at a strain rate of 10^{-3} s^{-1} on a screw-driven machine. The results of these tests are reported elsewhere [9, 14, 40].

2.2. APT Data Acquisition

Following room-temperature mechanical testing, standard metallography techniques were used to mechanically polish single fractured half tensile specimens for focused ion beam (FIB) sample preparation. Atom probe needles were prepared using the FIB lift-out method [41] from the non-deformed head areas of the half tensile specimens at the Low Activation Materials Development and Analysis facility at ORNL using an FEI Quanta 3D dual-beam FIB [42]. Liftouts were prepared from each of the four FeCrAl compositions at the 7.0 dpa condition in addition to the unirradiated, 0.8 dpa and 1.8 dpa conditions of the Fe-18Cr-5.8Al composition. All specimens were mounted on silicon microtip coupons. Samples were analyzed using a Cameca Instruments Local Electrode Atom Probe (LEAP) 4000X HR at either the Center for Nanophase Materials Sciences at ORNL or the Microscopy and Characterization Suite (MaCS) at the Center for Advanced Energy Studies (CAES).

All sharpening was performed using a 30 kV Ga ion beam with a 5 kV final milling step to minimize Ga implantation. Sharpened microtips were transferred promptly from the FIB into the LEAP to minimize sample oxidation and degradation in air. The LEAP was operated in the laser-pulsed mode at a base specimen temperature of 50 K, pulse repetition rate of 200 kHz and a laser energy of 50 pJ. The detection rate was typically set at 0.5%. Data sets with at least 10 million ions were collected from a minimum of two

tips for each condition. The atom probe data was reconstructed and analyzed using the Integrated Visualization & Analysis Software (IVAS 3.6.8).

The α' precipitates were analyzed using the maximum-separation cluster-finding algorithms packaged with the IVAS software [43–46]. The two primary inputs to this algorithm are the maximum separation distance, d_{max} — defining the distance at which Cr atoms can be considered to belong to the same precipitate, and minimum cluster size, N_{min} — defining the smallest number of atoms that can define a statistically significant precipitate. The values of d_{max} and N_{min} were chosen in such a way as to identify only precipitates of statistical significance by comparing the nearest-neighbor distribution and cluster size distributions to that of a randomly generated data set [21, 43, 47]. Careful selection of these parameters is essential for an accurate analysis, as improper values will result in either inclusion of artificially generated precipitates or omission of precipitate clusters that are statistically significant. Once precipitates have been identified by the algorithm, their sizes and compositions can be analyzed and the number density of precipitates in the irradiated matrix can be determined.

The radius of the α' precipitate clusters ($R_{\alpha'}$) was calculated based on the number of atoms detected in each precipitate using the spherical equivalent radius [21, 48] with an assumed atom probe detection efficiency of 0.36 for the Cameca LEAP 4000X HR and an atomic density for the α' phase assumed to be identical to that of α -Fe (84.3 atoms nm⁻³). Although the cluster compositions were drastically different from those of α -Fe, recent energy-filtered transmission electron microscopy and high-resolution transmission electron microscopy investigations have shown that the α' phase is semi-

coherent and that the lattice parameter differs by only 0.01 Å between the two phases [49]; thus the atomic densities are similar. The number density ($N_{\alpha'}$) and volume fraction ($f_{\alpha'}$) of the α' precipitates were calculated using the methodology outlined by Bachhav et al. [21].

2.3. SANS Data Acquisition

A more extensive sample matrix of irradiated FeCrAl alloys was examined using SANS techniques. SANS data was acquired from the head region of fractured half tensile specimens using a 4 mm beam aperture on the CG-2 General-Purpose SANS beam line (GP-SANS) at HFIR [50]. Three detector distances were used for data collection — two using 0.472 nm neutrons at distances of 1.079 m and 7.779 m and one using 1.2 nm neutrons at a distance of 19.279 m. To maximize the accessible range of momentum transfer (Q), the detector was laterally offset by 0.4 m in each measurement. In total, measurements spanned a Q range of $0.01 < Q < 10 \text{ nm}^{-1}$. The data was converted to the cm^{-1} scale by correcting the medium-length data for thickness and transmission before normalizing to the attenuated direct beam. The data from the other two detector lengths was then scaled to match the medium-length data to generate the full, combined curves. All data was collected at room temperature. Multiple scattering corrections were deemed negligible. Fits to the experimental data assumed α' clusters to be spheres interacting with an exclusion volume [14].

3. Results and discussion

3.1. APT Data Analysis & Correction

An accurate quantitative analysis of FeCrAl APT data requires proper peak deconvolution in the time-of-flight (TOF) spectrum and correction for trajectory aberration artifacts. The necessity for peak deconvolution is a result of specific isotopes of the three primary alloying elements sharing peaks in the TOF spectrum for a given FeCrAl APT data set; specifically, the peak corresponding to a mass-to-charge ratio of 27 daltons (Da) contains counts from $^{27}\text{Al}^{1+}$, $^{54}\text{Cr}^{2+}$, and $^{54}\text{Fe}^{2+}$, and the peak at 54 Da contains counts from both $^{54}\text{Cr}^{1+}$ and $^{54}\text{Fe}^{1+}$. Since there is no current way to uniquely resolve the elemental identity of an ion causing a detector event in this range, all the counts in the multi-peak must be initially assigned to a single isotope.

In the present analysis, the counts in the 27 Da peak were assigned to $^{27}\text{Al}^{1+}$ and the counts in the 54 Da peak were assigned to $^{54}\text{Fe}^{1+}$. This resulted in an initially skewed compositional analysis that can be corrected using peak decomposition techniques. Although the IVAS software has a built-in peak decomposition algorithm, it assumes natural isotopic abundances when comparing the ratios of counts contained in known single isotope peaks on the TOF spectrum. As this assumption does not hold for a neutron-irradiated system in which transmutation and decay has occurred, the peak decomposition and composition correction were applied manually following the IVAS analysis using the methodology outlined in Larson et al. [51]. The expected isotopic abundances used for the decomposition of peaks were calculated using the ORIGEN-2.2 isotope generation and depletion code and were decay-corrected for the time of data collection for each

specimen [52].

A second consequence of this peak overlap was a conservative estimate for Cr clustering since detector events for $^{54}\text{Cr}^{2+}$ and $^{54}\text{Cr}^{1+}$ ions were initially identified as $^{27}\text{Al}^{1+}$ and $^{54}\text{Fe}^{1+}$, respectively, in the reconstruction and subsequent cluster-finding analysis. However, these events were expected to make up less than 4.2% of the total Cr detector events (based on the adjusted isotopic abundance of ^{54}Cr); therefore, this effect was expected to be minimal. Finally, some Cr was lost following irradiation owing to neutron capture of ^{50}Cr resulting in transmutation to ^{51}Cr and subsequent decay to ^{51}V ($t_{1/2} = 27.7d$). However, the observed bulk V content was found to be less than 0.1 at.% in all specimens studied, so it was assumed that this effect could also be neglected.

Trajectory aberration artifacts manifest as density "hot spots" in the atom probe reconstructions in the vicinity of Cr-rich precipitates, though no appreciable physical density difference is expected between the two phases. This artificial densification is expected when a low-field precipitate phase, such as α' ($F_{Cr} = 29$ V/nm) is embedded in a high-field matrix, such as α -Fe ($F_{Fe} = 33$ V/nm) [53]. A 2-dimensional density heat map illustrating this phenomenon is shown in Figure 1. In order to correct for this, the extra ions in the denser regions were assumed to have originated in the matrix α -Fe phase, artificially enriching the precipitates in Fe while simultaneously increasing their apparent size (based on the spherical equivalent radius assumption). The precipitate composition and radii can then be corrected by quantifying the magnitude of this density change and removing excess ions in a proportion commensurate with the matrix composition. Density was

analyzed by parsing APT data sets into cubic bins and then comparing bin densities in precipitate volumes with those in matrix volumes. Applying the composition correction accordingly yielded phase compositions that are comparable to those previously reported in the literature [21, 23, 37]. Additionally, this technique accounted for aberration effects on a specimen-wide scale compared with the usual treatment of examining composition proxigrams for a few select precipitates [21, 37, 54].

The unirradiated Fe-18Cr-5.8Al specimen was analyzed to serve as a representative sample of the alloys in their as-received state to assess whether clustering was present in these materials before irradiation. Evidence of statistically significant clustering was not observed in the atom maps, nearest neighbor distribution analyses, concentration isosurfaces, or χ^2 statistical analyses [53, 55] generated from this data set.

Indications of Cr clustering were present in all irradiated specimens analyzed regardless of dose or composition both before and after applying the discussed analysis and correction techniques to the raw data sets. A summary of the results of the atom probe analysis — including the final matrix and precipitate compositions and precipitate morphology data for all compositions and irradiation conditions studied — is given in Table 3. Representative atom probe reconstruction data depicting precipitate morphologies for each composition irradiated to 7.0 dpa are shown in Figures 2 and 3. Precipitates are represented using the indexed cluster maps generated by the cluster-finding algorithm (Figure 2) and by displaying 20 nm thick Cr atom maps (Figure 3). Application of the Langer-Baron-Miller method to these irradiated data sets confirmed that the observed microstructures display no

indication of precipitation occurring via a spinodal decomposition mechanism [56].

The quantitative work performed on these particular specimens attempts to improve on the results of Edmondson et al. [15], in which isotope generation and decay and trajectory aberration effects were not accounted for in calculating precipitate composition and size. Figure 4 presents a comparison of the calculated matrix and precipitate Cr contents for each alloy at 7.0 dpa from Edmondson et al. to the present work. Note that accounting for nuclear reactions and transmutations in the FeCrAl system had a marginal effect on reported composition. However, although the effect of transmutation was negligible in this instance, it may have a greater impact in systems for which different irradiation conditions are employed (higher fluences, different reactor neutron spectra) or in systems containing isotopes with higher neutron absorption cross sections. However, compensating for trajectory aberrations affected the reported results drastically. Therefore, both of these effects should be considered in analyzing APT results for neutron-irradiated specimens. As a result of these phenomena, the extent to which Al additions destabilized the α' phase was previously exaggerated [15]. Here, precipitate compositions ranged from ~ 58 at.% Cr for low-Cr, high-Al alloys to ~ 89 at.% Cr for high-Cr, low-Al alloys. The latter are similar to the ~ 85 at.% Cr precipitates reported in binary Fe-Cr alloys [21]. In addition, the previously reported partitioning of Al to the α -Fe phase is still shown to occur [15].

The damage dose evolution of α' precipitation in neutron-irradiated FeCrAl has not been reported previously. Note that the uninstrumented rabbit irradiation methods used in this study introduce some variation in the

irradiation temperatures of these specimens that may have affected the observed trends. Representative atom probe reconstructions illustrating the progression of α' precipitation for the various dose conditions studied for the Fe-18Cr-5.8Al alloy are shown in Figures 5 (indexed clusters) and 6 (atom maps). Significant precipitation was observed for all three dose conditions. In the lowest-dose specimen (0.8 dpa), a high number density of smaller, less mature (as indicated by composition) precipitates were observed. The volume fraction of precipitates increased in the 1.8 dpa specimen (which was also subject to the highest irradiation temperature — see Table 2); that result was accompanied by a decrease in precipitate number density and an increase in average precipitate radius. Volume fraction was not appreciably changed by continued irradiation to 7.0 dpa, whereas the number density was seen to decrease as the precipitate radius increased, suggesting a transition to a possible coarsening regime past 1.8 dpa.

3.2. SANS Model Fitting & Quantification

Plots comparing scattering intensities for $Q \geq 0.5 \text{ nm}^{-1}$ for the 7.0 dpa FeCrAl alloy compositions are shown in Figure 7a. A similar plot is shown in Figure 7b comparing the scattering intensities for the various irradiation conditions of the model Fe-18Cr-5.8Al alloy. Changes in the scattering intensity are clearly observed both for increasing alloy Cr content with constant dose and for increasing irradiation dose with constant alloy composition. These intensity trends are similar to those seen in other SANS investigations of α' precipitation in aged FeCrAl alloys and irradiated FeCr alloys by several authors [14, 22, 32, 33, 57, 58]. This qualitative agreement validates our use of the spherical exclusion model to assess α' precipitation in the SANS data.

SANS scattering intensity can be modeled by assuming α' precipitates to be monodisperse spheres interacting with the α matrix using a hard-sphere potential. This approximation assumes the α' precipitate forms a depletion zone that is devoid of other precipitates in its immediate vicinity. This appears to be a reasonable assumption based on APT reconstructions. The absolute scattering intensity then takes the following functional form:

$$I(q) = V \eta_{\alpha'} \Delta \rho^2 P(q, r) S(q, R_{hs}, \eta_{hs}) \quad (1)$$

where $\eta_{\alpha'}$ is the volume fraction of α' precipitates, $\Delta \rho$ is the difference in the scattering length densities between the precipitate phase and the matrix, V is the volume of the precipitates, $P(q, r)$ is the particle form factor for spherical precipitates, and $S(q, R_{hs}, \eta_{hs})$ is the hard-sphere structure factor describing scattering interference between particles. The functional forms of both the form and structure factors can be found in Pedersen [59]. An additional contribution in the residual background can be observed from large impurities or precipitates in metallic alloys, which can be approximated using a low- q power law [60]. $I(q)$ can thus be rewritten as:

$$I(q) = V \eta_{\alpha'} \Delta \rho^2 P(q, r) S(q, R_{hs}, \eta_{hs}) + A q^{-m} + B \quad (2)$$

where A is the power law length scale factor, m is the power law exponent, and B is the background. By grouping the prefactors into a single scale factor constant:

$$I_0 = \eta_{\alpha'} \Delta \rho^2 \quad (3)$$

these models can be fit to the experimental data using a modified Levenberg-Marquardt algorithm where initial guesses for the seven fitting parameters

and the q -range for fitting are optimized to produce the best model representation of the experimental data.

Other values of interest can be determined using the parameters determined from the hard-sphere model. The precipitate volume fraction, $\eta_{\alpha'}$, can be determined from [61]:

$$\eta_{\alpha'} = \frac{\eta_{hs}}{(R_{hs}/r)^3} \quad (4)$$

while the precipitate number density can be calculated from [61]:

$$N = \frac{3\eta_{\alpha'}}{4\pi r^3} \quad (5)$$

The statistical error of the fitting parameters and resulting volume fraction and number density quantification is on the order of 10%.

In addition, the α' precipitate composition can be estimated by using the known initial Cr content in the as-received FeCrAl alloy and the calculated precipitate volume fraction by extracting the scattering length density difference, $\Delta\rho$, from the scale factor, I_0 . As discussed previously, the relative difference in the unit cell dimension between the two phases is 0.01 Å [49] and the scattering length difference between Al and Cr is minor in comparison to Cr and/or Al to Fe (b_{Al} : 3.449×10^{-15} m, b_{Cr} : 3.635×10^{-15} m, b_{Fe} : 9.45×10^{-15} m). Atom probe studies of α' precipitates in irradiated and aged FeCrAl alloys [15, 35–37], including this one, have shown small variances in the Al content between the matrix and precipitate phases, making the contrast contributions due to Al relatively minor. The result is that the major contributions to the scattering length density difference can be assumed to be due to the relative Cr content of the α' precipitates to the α -Fe matrix. Thus, the Cr content of the α -Fe matrix can be approximated using [61, 62]:

$$C_{Cr}^{matrix} = \bar{C}_{Cr} - \frac{\eta_{\alpha'} \Delta \rho a_0^3}{4(b_{Fe} - b_{Cr})} \quad (6)$$

where $\bar{C}_{Cr}$ is the bulk composition of Cr (at.%), C_{Cr}^{matrix} is the α -Fe matrix Cr composition (at.%), and a_0 is the lattice parameter (2.87 Å). The Cr content of the precipitates can then be determined using the calculated precipitate volume fraction, $\eta_{\alpha'}$:

$$C_{Cr}^{\alpha'} = [\bar{C}_{Cr} - (1 - \eta_{\alpha'}) C_{Cr}^{matrix}] / \eta_{\alpha'} \quad (7)$$

It should be noted that this calculation is dependent on both the statistical error of the fitting parameters and the systematic errors including the absolute scale of the data, neglecting the contrast contributions due to Al, and approximating a polydisperse system with a monodisperse model. An identical model has been applied to precipitation of δ' phase in Al-Li alloys (a polydisperse system), and errors in the composition of precipitates were on the order of 15-30% [61]. It should also be noted that reported compositions are sensitive to $\eta_{\alpha'}$ and break down for extremely low volume fractions due to both uncertainty and expected poor scattering contrast between the matrix and precipitate phases. In addition, the calculation assumes a coarsening regime. As such, reported precipitate compositions for low dose conditions are not anticipated to be accurate.

Table 4 summarizes the calculated α' precipitate morphologies resulting from the aforementioned analysis. It should be noted that the reported error is either the standard error of the coefficient using the nonlinear least squares estimation of the model for those values determined directly through the fitting procedure; or the propagation of the standard error of the coefficients

used in the calculation of the values not determined directly through fitting. As such, these errors only represent the error in the fitting analysis and do not provide direct insight into the repeatability of the SANS experiments.

Data for the 1.8 dpa specimens were reported previously by Field et al. [14] by using a simplified model fit with a scattering length density difference calculated by assuming precipitate compositions of Fe-81.3Cr-4.7Al (wt.%) as observed by Capdevila et al. [37]. The APT cluster composition analysis and the SANS derived compositions from Eq. 6 and Eq. 7 presented herein makes it clear that the compositions assumed previously were not physical for the alloys currently being studied. Using these composition-independent models should result in a more physical interpretation of the SANS data.

3.3. APT & SANS Data Comparison & Discussion

In comparing the analysis of precipitate morphologies between the APT and the SANS results, it became clear that, while qualitative trends are preserved, there is some disparity between the reported quantitative values. These differences can be attributed to a variety of factors associated with assumptions and uncertainties inherent in each of these analysis techniques.

First, both techniques were unable to resolve small clusters. SANS has an instrument-dependent physical resolution limit for observed cluster diameters that is usually in the range of 0.5–1.5 nm [63, 64]. APT is able to resolve precipitates smaller than this, but clusters that are on the same length scale as those found as a result of composition fluctuations in a random solid solution are not considered. It is expected that this would result in the average radius reported by SANS being slightly larger than the precipitate

size reported by APT, which is consistent with the present findings.

Analysis of the SANS data assuming a monodisperse precipitate size distribution is also clearly not physical. Attempts were made to fit more complex polydisperse models to the data, but good fits were not able to be achieved for all conditions and the resulting quantification for those cases appeared nonsensical. However, while the monodisperse model is an oversimplification of the system, its analytical merit is supported by reasonable agreement with present APT results and by previous studies of precipitates in the Al-Li system by Pedersen in which both monodisperse and polydisperse models were applied with comparable results [61].

Furthermore, a number of artifacts can affect the accuracy of the APT measurements, including local magnification effects and surface migration of solute atoms [53, 65], in addition to the previously mentioned trajectory aberrations, TOF peak overlap, and neutron transmutation effects that were accounted for in the present analysis. Quantification of precipitate morphologies using the maximum separation algorithms can also be very sensitive to the input parameters used [43, 46].

Finally, the present SANS analysis assumed pure nuclear scattering and ignored magnetic scattering contributions. As the ferritic α -Fe matrix was plainly ferromagnetic (although the α' phase precipitates are not, according to [66]), this assumption was clearly inadequate. However, it is very difficult to rigorously compensate for this magnetism analytically; therefore, SANS data collection for these types of alloys is usually conducted in a saturated magnetic field, allowing for the separation of the nuclear and magnetic scattering contributions to the SANS intensity. Assuming pure nuclear scat-

tering in the presence of magnetic scattering, as was done in this study, was expected to result in inflated values for number density and volume fraction. A more detailed discussion of some of the challenges of comparing SANS and APT results is presented in the context of reactor pressure vessel steel precipitate characterization by Hyde et al. [64].

Despite the quantitative disagreements in the two data sets, values are generally on the same order of magnitude and the agreement between the observed trends lends additional confidence to these findings. A high density of smaller α' precipitates formed initially at low doses, and these precipitates coarsened over time with increasing dose. Increasing Cr content generally resulted in higher number densities and volume fractions of precipitates. As demonstrated by Figure 8, these general trends agree with the results of past studies on aged and irradiated binary FeCr alloys [20–24, 47, 67–69] and studies of aged FeCrAl alloys by Cook et al. and Messoloras et al. [32, 33]. However, the spread in the reported data reinforces the importance of systematic studies of α' precipitation in high-Cr ferritic alloys. Variations in alloy composition, aging or irradiation temperature, time at temperature, and even measurement technique (as discussed prior) have resulted in reported precipitate number densities that span three orders of magnitude, and the number of variables involved can make direct comparison between studies challenging. For example, the composition of the materials investigated by Messoloras et al. are arguably similar to the model alloys studied here, yet the number densities they report are far lower in comparison, which can be attributed to differences in material treatment (aged vs. irradiated, both at different temperatures) and in the models used to reduce and fit the SANS

data [33].

All observed experimental evidence appears to support precipitation in these FeCrAl alloys by a nucleation and growth mechanism. Isolated precipitates as opposed to percolated microstructures were observed in APT reconstructions, and application of the Langer-Baron-Miller method failed to identify a spinodal decomposition regime. Additionally, good fits are achieved between the experimental data and the employed SANS models, which assume isolated spherical precipitates. Based on these observations, and the fact that the considered alloys reside in the composition range for nucleation and growth based on the thermodynamic models of Capdevila et al. [35, 37], it is concluded that all materials studied herein undergo precipitation by the nucleation and growth mechanism during elevated temperature neutron irradiation in the range of 320–382°C.

Based on the α - α' ternary phase boundary proposed by Kobayashi et al. [34], precipitation is not necessarily expected to occur in the Fe-10Cr-9.3Al and Fe-12Cr-8.7Al alloys studied herein, but indications of Cr clustering in these materials are observed in both the APT and SANS investigations. However, this phase boundary is based solely on change in Vickers hardness (ΔH_V) and not on direct observation of precipitate microstructure — thus, it is possible that the precipitates in these alloys are not contributing significantly to the increase in hardness. The less Cr-rich precipitate compositions observed may serve to reduce the defect barrier strength, as speculated by Edmondson et al. [15], and the decreased precipitate densities observed are expected to result in a diminished hardening response in accordance with the dispersed barrier hardening model [70]. The change in yield strength ($\Delta\sigma_y$)

associated with α' precipitates in the Fe-10Cr-9.3Al and Fe-12Cr-8.7Al alloys in the 1.8 dpa condition was determined to be 75 and 200 MPa, respectively, by Field et al. [14]. Assuming $\Delta\sigma_y$ can be related to the change in hardness by $\Delta\sigma_y = 3.06\Delta H_V$ for ferritics according to Busby et al. [71], the expected ΔH_V is expected to fall between 25 and 65 kg/mm², both of which are very close to the arbitrary boundary drawn by Kobayashi at 50 kg/mm². Furthermore, the materials investigated by Kobayashi et al. did not contain Y additions, which have been shown to enhance the rate of embrittlement in similar systems [33]. The proposed boundary is defined for an aging temperature of 475°C, while the investigated materials were irradiated at temperatures between 320 and 382°C. The diminished Cr solubility at these lower temperatures may be sufficient to induce α' precipitation in these less Cr-rich alloys in current work.

Substantial work has been performed on characterizing precipitates in the PM 2000TM (nominal composition Fe-18.5 at.% Cr-10.10 at.% Al + Ti,Y) commercial oxide dispersion-strengthened (ODS) FeCrAl alloy by Capdevila et al. [35–37, 55, 72]. The partitioning of Al to the matrix phase observed in the current work was also observed in PM 2000TM. However, the commercial alloys did not exhibit the reduced precipitate Cr contents at saturation seen in the model alloys investigated here. While a number of differences exist between the two studies, Capdevila et al. did report significant changes in phase composition as a function of aging time and temperature [37] which may suggest that the precipitates in the alloys with lower Cr contents and higher Al contents required more time at temperature/irradiation dose to mature. However, precipitate compositions for binary Fe-Cr alloys reported

by Bachhav et al. appeared to approach theoretical saturation values after irradiation to just 1.82 dpa at 290°C [21]. As this study achieved doses beyond this, one might conclude that Al may not suppress the equilibrium phase composition, but may instead retard the precipitate maturation kinetics. Unfortunately, as neither Cr nor Al content are held constant in the materials used in this study, further systematic investigation is required in order to reach a decisive conclusion on this matter.

Additional insight into the kinetics of the coarsening behavior of the α' precipitates in the FeCrAl alloy system can be gained by looking at the SANS results in the context of the Umantsev-Olson-Kuehmann-Voorhees (UOKV) model [73, 74]. The UOKV model is an adaptation of the diffusion-limited coarsening model for binary alloys developed by Lifshitz and Slyozov [75] and Wagner [76] (LSW model) for ternary alloy systems. Both of these models make use of a set of fundamental assumptions [77, 78]: (1) both terminal phase states are dilute solutions, so that a linearized version of the Gibbs-Thomson equation is valid; (2) the precipitated volume fraction is close to zero, so that interparticle interactions can be neglected; (3) the precipitated volume fraction is constant, i.e., the model applies to the late stages of precipitation in which the matrix is no longer supersaturated; (4) coarsening occurs in a stress-free matrix; and (5) precipitates have a spherical morphology. The ultimate conclusion of the LSW and UOKV models is that precipitate coarsening with time can be described by the following temporal power laws:

$$\overline{R}_{\alpha'}(t) = K_R t^{1/3}, \quad (8)$$

$$N_{\alpha'}(t) = K_N t^{-1}, \quad (9)$$

$$\Delta c(t) = K_C t^{-1/3}, \quad (10)$$

where $\Delta c(t)$ is the solute saturation in the matrix (difference between matrix solute content at time t and the equilibrium matrix solute content) and K_R , K_N , and K_C are rate constants for the radius, number density, and solute composition evolution, respectively.

Figures 9a and 9b plot average precipitate radius and number density, respectively, based on the current SANS investigation versus time at temperature (i.e., irradiation time). Figure 9a demonstrates that cluster radius temporal evolution in the FeCrAl materials studied gives a reasonable fit to the power law functional form predicted by the UOKV model. Furthermore, the slope of these curves is shown to increase with increasing Cr content, corresponding to an increasing rate constant for radius evolution, which is to be expected as the driving force for precipitation increases. Note that the 1.8 dpa specimen, which was irradiated at a higher temperature, consistently shows increased coarsening kinetics in this plot. However, Figure 9b shows that the rate of decay in the experimentally observed number densities with time is somewhat less than model predictions. Similar behavior was shown by Novy et al. for α' precipitation in a Fe-20Cr alloy thermally-aged at 500°C in which the time exponent trended toward the expected -1 only after long aging times. This transient coarsening regime was explained as an overlap between nucleation, growth, and coarsening, as first proposed by Robson [79]. It seems reasonable to assume that the irradiated FeCrAl alloys are exhibiting a similar behavior, though it is impossible to definitively assess the transient nature of the regime with only three dose data points per

specimen and varying capsule irradiation temperatures. Note that the Fe-10Cr-9.3Al exhibits increasing precipitate number density with dose/time, suggesting that this alloy is still in a nucleation and growth regime through 7 dpa.

Assuming that the behavior is indeed similar, two statements can be made based on the demonstrated experimental agreement with predicted behavior: (1) α' precipitation in irradiated FeCrAl is likely a diffusion-limited phenomenon, and (2) the mechanism for precipitation is similar in thermally aged and irradiated FeCr and FeCrAl alloys. In comparing experimental fits to the LSW/UOKV models from the present work with data reported by Novy [23] and for Fe-15.7Cr-9.7Al-0.19Y (at.%) aged at 475°C reported by Messoloras [33] it is shown that both aging experiments yield higher rate constants for radius evolution than the irradiated alloys presented herein. This suggests that thermal aging experiments can be used to provide insight into precipitation phenomena in the irradiated system, especially if some rigor is applied to determine the temperature shift required to emulate a given irradiation condition.

4. Conclusions

In summary, four model FeCrAl alloys were fabricated and irradiated in HFIR to various fluences, resulting in damage levels of up to 7.0 dpa. Independent but complementary analyses of the resulting α' precipitate morphology have been performed using APT and SANS techniques. Qualitative agreement was demonstrated between the two data sets and the dose and composition trends identified were found to be similar to those seen in previ-

ous studies of aged Fe-Cr-Al alloys, and for aged and irradiated binary Fe-Cr systems and commercial ferritic alloys. Based on the presented analysis, the following conclusions can be drawn:

- Performing SANS and APT experiments in tandem can help overcome the individual limitations of each technique, but achieving reasonable agreement requires careful consideration of the assumptions involved in the analysis. Artifacts in APT data, specifically trajectory aberration artifacts, must be accounted for to accurately determine precipitate character, while the impact of the simplifying approximations utilized by a chosen SANS model must be taken into account when interpreting results.
- The severity of the precipitation response scaled with the alloy Cr content, as expected. Al additions appeared to partially destabilize the α' phase, ultimately resulting in reduced Cr content in the α' phase (down to 58 at.% Cr, as indicated by APT results) compared with results reported in studies on the binary Fe-Cr system (85+ at.% Cr) by either changing the equilibrium phase composition or by retarding precipitate maturation kinetics. Furthermore, Al was shown to partition to the α -Fe matrix, being preferentially rejected from the precipitate volume.
- Precipitate nucleation appears to proceed rapidly, entering a coarsening regime before 1.8 dpa in the current study. Reasonable fits of the presented SANS data to the UOKV model predictions indicate similar transient coarsened behavior to previous studies of α' precipitates in an

aged Fe-Cr alloy and suggest that α' precipitation is a diffusion-limited process and that precipitation in irradiated systems can be adequately pre-screened using thermal aging experiments.

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Table 1: FeCrAl alloy compositions in both at.% and wt.% [14, 15].

Alloy		Fe	Cr	Al	Y	C	S	O	N	P	Si
Fe-10Cr-9.3Al	at.%	bal.	10.15	9.34	0.023	0.022	0.0016	0.0043	0.0011	0.010	<0.02
	wt.%	bal.	10.01	4.78	0.038	0.005	0.0010	0.0013	0.0003	0.006	<0.01
Fe-12Cr-8.7Al	at.%	bal.	12.16	8.66	0.016	0.022	0.0021	0.0056	0.0034	0.0	0.02
	wt.%	bal.	11.96	4.42	0.027	0.005	0.0013	0.0017	0.0009	0.0	0.01
Fe-15Cr-7.7Al	at.%	bal.	15.33	7.70	0.021	0.022	0.0007	0.0083	0.0026	<0.003	0.02
	wt.%	bal.	15.03	3.92	0.035	0.005	0.0004	0.0025	0.0007	<0.002	0.01
Fe-18Cr-5.8Al	at.%	bal.	18.00	5.81	0.010	0.022	0.0010	0.0050	0.0042	<0.003	<0.02
	wt.%	bal.	17.51	2.93	0.017	0.005	0.0006	0.0015	0.0011	<0.002	<0.01

Table 2: Summary of irradiation conditions for each irradiation target capsule irradiated in HFIR.

Capsule ID	Exposure	Neutron Flux	Neutron Fluence	Dose Rate (dpa/s)	Dose (dpa)	Irradiation Temperature (°C)
	Time	(n/cm ² s)	(n/cm ²)			
	(hrs)	E > 0.1 MeV	E > 0.1 MeV			
FCAY-01	120	8.54×10^{14}	3.69×10^{20}	7.7×10^{-7}	0.3	334.5 ± 0.6
FCAY-02	301	8.54×10^{14}	9.25×10^{20}	7.7×10^{-7}	0.8	355.1 ± 3.4
FCAY-03	614	8.84×10^{14}	1.95×10^{21}	8.1×10^{-7}	1.8	381.9 ± 5.4
FCAY-04	2456	8.74×10^{14}	7.73×10^{21}	7.9×10^{-7}	7.0	319.9 ± 12.7

Table 3: Summary of results of APT analysis of α' precipitates for all compositions and dose conditions studied. Compositions are given in at.%

Alloy	Irradiation Dose (dpa)	Irradiation Temp (°C)	Matrix Composition			Mean Cluster Composition			$N_{\alpha'}$ ($\times 10^{24} \text{ m}^{-3}$)	$f_{\alpha'}$ (%)	$\bar{R}_{\alpha'}$ (nm)
			Fe	Cr	Al	Fe	Cr	Al			
Fe-10Cr-9.3Al	7.0 dpa	319.9 $\pm$ 12.7	80.99	9.26	9.54	31.19 $\pm$ 8.39	64.88 $\pm$ 9.56	3.80 $\pm$ 2.47	0.51 $\pm$ 0.11	1.78 $\pm$ 0.45	1.49 $\pm$ 0.90
Fe-12Cr-8.7Al	7.0 dpa	319.9 $\pm$ 12.7	80.69	10.61	8.57	37.10 $\pm$ 6.24	58.22 $\pm$ 6.65	4.52 $\pm$ 1.46	0.69 $\pm$ 0.01	3.24 $\pm$ 0.20	1.82 $\pm$ 0.84
Fe-15Cr-7.7Al	7.0 dpa	319.9 $\pm$ 12.7	80.30	11.91	7.60	22.71 $\pm$ 7.62	73.71 $\pm$ 8.07	3.45 $\pm$ 1.61	2.2 $\pm$ 0.11	5.79 $\pm$ 0.41	1.57 $\pm$ 0.62
Fe-18Cr-5.8Al	0.8 dpa	355.1 $\pm$ 3.4	79.11	14.90	5.90	27.84 $\pm$ 6.05	69.62 $\pm$ 6.30	2.48 $\pm$ 1.00	3.1 $\pm$ 0.03	5.70 $\pm$ 0.21	1.50 $\pm$ 0.41
	1.8 dpa	381.9 $\pm$ 5.4	80.61	13.21	6.07	18.25 $\pm$ 6.81	79.52 $\pm$ 7.17	2.16 $\pm$ 1.05	2.9 $\pm$ 0.31	7.44 $\pm$ 0.73	1.58 $\pm$ 0.51
	7.0 dpa	319.9 $\pm$ 12.7	80.61	13.13	6.02	8.49 $\pm$ 7.02	89.22 $\pm$ 7.41	2.18 $\pm$ 1.29	1.9 $\pm$ 0.06	6.72 $\pm$ 1.73	1.78 $\pm$ 0.66

Table 4: Summary of results of SANS analysis of α' clustering for all composition and dose conditions studied.

Alloy	Irradiation Dose (dpa)	Irradiation Temp (°C)	$N_{\alpha'}$ ($\times 10^{24} \text{ m}^{-3}$)	$f_{\alpha'}$ (%)	$\bar{R}_{\alpha'}$ (nm)	C_{Cr}^{matrix}	$C_{Cr}^{\alpha'}$
						(at.%)	(at.%)
Fe-10Cr-9.3Al	0.8 dpa	355.1 $\pm$ 3.4	0.0167 $\pm$ 0.00535	0.06 $\pm$ 0.019	2.03 $\pm$ 0.03	10.1 $\pm$ 0.02	126.5 $\pm$ 55.43
	1.8 dpa	381.9 $\pm$ 5.4	0.0275 $\pm$ 0.00759	0.12 $\pm$ 0.034	2.18 $\pm$ 0.03	10.0 $\pm$ 0.03	95.4 $\pm$ 35.05
	7.0 dpa	319.9 $\pm$ 12.7	0.174 $\pm$ 0.0476	0.99 $\pm$ 0.266	2.40 $\pm$ 0.05	10.0 $\pm$ 0.05	25.2 $\pm$ 6.13
Fe-12Cr-8.7Al	0.3 dpa	334.5 $\pm$ 0.6	1.59 $\pm$ 0.115	1.65 $\pm$ 0.109	1.37 $\pm$ 0.01	11.5 $\pm$ 0.05	52.1 $\pm$ 4.05
	1.8 dpa	381.9 $\pm$ 5.4	0.512 $\pm$ 0.0449	1.42 $\pm$ 0.121	1.83 $\pm$ 0.01	11.3 $\pm$ 0.08	70.0 $\pm$ 7.49
	7.0 dpa	319.9 $\pm$ 12.7	0.335 $\pm$ 0.0773	1.33 $\pm$ 0.304	2.13 $\pm$ 0.02	11.7 $\pm$ 0.12	45.6 $\pm$ 11.58
Fe-15Cr-7.7Al	0.3 dpa	334.5 $\pm$ 0.6	4.39 $\pm$ 0.269	2.76 $\pm$ 0.149	1.16 $\pm$ 0.01	13.4 $\pm$ 0.12	82.3 $\pm$ 5.59
	1.8 dpa	381.9 $\pm$ 5.4	1.23 $\pm$ 0.0542	3.08 $\pm$ 0.126	1.81 $\pm$ 0.01	13.4 $\pm$ 0.09	75.0 $\pm$ 3.76
	7.0 dpa	319.9 $\pm$ 12.7	0.706 $\pm$ 0.0692	3.06 $\pm$ 0.291	2.15 $\pm$ 0.02	13.9 $\pm$ 0.15	60.6 $\pm$ 6.60
Fe-18Cr-5.8Al	0.8 dpa	355.1 $\pm$ 3.4	2.81 $\pm$ 0.158	4.11 $\pm$ 0.200	1.52 $\pm$ 0.01	15.3 $\pm$ 0.16	82.1 $\pm$ 4.90
	1.8 dpa	381.9 $\pm$ 5.4	1.60 $\pm$ 0.0732	4.19 $\pm$ 0.174	1.85 $\pm$ 0.01	15.3 $\pm$ 0.13	79.4 $\pm$ 3.96
	7.0 dpa	319.9 $\pm$ 12.7	0.728 $\pm$ 0.0715	4.92 $\pm$ 0.467	2.53 $\pm$ 0.02	15.6 $\pm$ 0.26	64.6 $\pm$ 6.86

Figure 1: Representative atom probe 2-dimensional density heat map for Fe-18Cr-5.8Al irradiated to 7.0 dpa at 320°C. The hot spots indicative of an increased density of detector events were observed to be co-located with α' precipitates. Map generated from reconstructed data using a z-direction thickness of 4 nm with an x,y bin size of 0.5 nm.

Figure 2: Representative APT reconstructions for the various compositions of FeCrAl irradiated to 7.0 dpa at 320°C (2456 hrs at temperature), in which a color is assigned to each α' precipitate detected using the maximum-separation method cluster-finding algorithm native to IVAS. Figures are cropped to $50 \times 50 \times 100$ nm volumes to allow for direct comparison.

Figure 3: Representative Cr atom maps show evidence of clustering in all FeCrAl compositions studied when irradiated to 7.0 dpa at 320°C (2456 hrs at temperature). Maps represent a specimen thickness of 20 nm.

Figure 4: Comparison of reported matrix and cluster Cr contents for the four 7.0 dpa FeCrAl specimens resulting from standard IVAS peak decomposition techniques ("Uncorrected," from [15]) and from manual peak decomposition after accounting for isotope generation and decay, followed by accounting for trajectory aberrations through reconstruction density analysis ("Corrected," from present work). Error bars denote one standard deviation for precipitate composition.

Figure 5: Representative APT reconstructions for the various irradiation conditions studied for Fe-18Cr-5.8Al, in which a color is associated with each α' precipitate detected using the maximum-separation method cluster-finding algorithm native to IVAS. Figures are cropped to $50 \times 50 \times 100$ nm volumes.

Figure 6: Representative Cr atom maps illustrate the progression of α' precipitation in Fe-18Cr-5.8Al as radiation dose is increased up to 7.0 dpa.

Figure 7: Scattering intensities of model FeCrAl specimens obtained by SANS analysis after irradiation, (a) for varying alloy contents irradiated to 7.0 dpa at 320°C, and (b) for varied irradiation conditions for the Fe-18Cr-5.8Al alloy composition. Symbols indicate experimental data points, where lines indicate model fitting results.

Figure 8: Comparison of SANS data from the current study with results published in literature for various aged and irradiated Fe-Cr and Fe-Cr-Al alloys [20–29, 33]. Data points are color-coded by source and were determined through SANS investigations unless otherwise indicated.

Figure 9: Comparison of precipitate coarsening trends based on the three dose data points for each condition with behavior predicted by the LSW/UOKV models. Reasonable fits to the SANS results are achieved, with the plot shown in (a) demonstrating $\bar{R}_{\alpha'} \propto t^{1/3}$ and (b) demonstrating $N_{\alpha'} \propto t^{-1}$ for the irradiated FeCrAl alloys. Dashed lines indicate least squares fit of present data to predicted model trends for each FeCrAl composition studied. Error bars are generally on the same order of magnitude as the symbol height and thus have been omitted for clarity.