Irradiation-Enhanced α' Precipitation in Model FeCrAl Alloys

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Abstract

Model FeCrAl alloys with varying compositions (Fe(10–18)Cr(10–6)Al at.%) have been neutron irradiated at ~ 320 °C to damage levels of ~ 7 displacements per atom (dpa) to investigate the compositional influence on the formation of irradiation-induced Cr-rich α' precipitates using atom probe tomography. In all alloys, significant number densities of these precipitates were observed. Cluster compositions were investigated and it was found that the average cluster Cr content ranged between 51.1 and 62.5 at.% dependent on initial compositions. This is significantly lower than the Cr-content of α' in binary FeCr alloys. Significant partitioning of the Al from the α' precipitates was also observed.

Keywords: APT, FeCrAl, alpha prime, neutron irradiation

Ferritic alloys that contain significant quantities of Cr (>9 at.%) are candidate materials for next generation nuclear reactors, in part due to their corrosion resistance. [1] Recently, ferritic alloys with enhanced corrosion resistance based around the ternary alloy FeCrAl have been proposed to be used as light water reactor (LWR) fuel cladding materials due to their higher oxidation resistance in high-temperature steam environments when compared to conventionally used zirconium-based alloys. [2–5] These alloys are currently under development to determine the optimum composition to maximize the aqueous corrosion and high-temperature oxidation resistance, while still maintaining reasonable performance with regards to mechanical properties, neutronics, and radiation tolerance. [2–9]

However, one major drawback for the use of high-Cr ferritic alloys in high temperature or nuclear environments at temperatures in the range of 300–400 °C is the unwanted formation of Cr-rich α' precipitates within the Fe-rich α matrix that have been observed in both FeCr binary and FeCrAl ternary alloys. [10–15] The accelerated formation of α' in binary alloys under neutron irradiation is also well established (see, for example [10, 11]). **Nonetheless**, there is little information in the literature as to the irradiation-accelerated formation of α' precipitates in FeCrAl ternary alloys. Information on the formation and behaviour of α' precipitates is important when evaluating the hardening and embrittlement response of these materials.

Presented here is atom probe tomography characterization of α' precipitates formed in neutron-

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irradiated FeCrAl alloys of varying composition. Particular effort is directed towards determining the composition of the α' precipitates, and how that compares to α' precipitates formed in binary FeCr alloys; and the influence of varying the initial bulk alloy compositions has on the formation, composition, number densities, and sizes of the α' precipitates.

The materials used in this study were a series of FeCrAl model alloys that had a Cr content that varied between 10 and 18 at.%. The materials were fabricated by arc melting the pure element feedstocks, followed by hot forging/rolling and a heat treatment. Further details of the fabrication route can be found elsewhere. [2, 5] The resultant microstructure was fully BCC with an average grain size of $\sim 20\text{-}30\text{ }\mu\text{m}$ for all alloys. [2, 5] Having a similar grain size across all alloys is critical in a study of this type, as it has recently been shown that the initial microstructure, in particular the initial grain size, may impact the formation rate of α' in thermally treated FeCrAl alloys. [13] The full compositions of the alloys used in this study are given in Table 1. These bulk compositions were determined from the atom probe tomography data, and are consistent with the previously reported values. [2, 5]

Table 1: Measured bulk compositions as determined through atom probe analysis using standard peak decompositions. The balance is Fe.

Alloy		Cr	Al	C	Co	Mg	Mn	N	O	S	V
Fe(10)CrAl	at.%	9.940	9.898	0.022	0.005	0.019	0.101	0.026	0.032	0.049	0.057
	wt.%	9.835	5.082	0.005	0.005	0.009	0.105	0.007	0.010	0.030	0.056
Fe(12)CrAl	at.%	11.827	8.656	—	0.008	0.014	0.124	0.025	0.019	0.024	0.070
	wt.%	11.634	4.418	—	0.009	0.007	0.129	0.007	0.006	0.014	0.068
Fe(15)CrAl	at.%	14.842	7.722	0.003	0.013	—	0.160	0.018	0.007	0.008	0.090
	wt.%	14.554	3.929	0.001	0.014	—	0.166	0.005	0.002	0.005	0.087
Fe(18)CrAl	at.%	17.511	6.324	0.035	0.009	0.027	0.094	0.014	0.033	0.049	0.101
	wt.%	17.080	3.202	0.008	0.010	0.012	0.097	0.004	0.010	0.029	0.097

Sheet-type, dogbone-shaped SS-J2-type specimens were cut from the bulk material and loaded into capsules for insertion into Oak Ridge National Laboratory’s (ORNL’s) High Flux Isotope Reactor (HFIR). Irradiations were conducted at a temperature of $319 \pm 10.2\text{ }^\circ\text{C}$ with a neutron flux of $8.74 \times 10^{14}\text{ n.cm}^{-2}.\text{s}^{-1}$ (equivalent to a dose rate of $7.9 \times 10^{-7}\text{ dpa.s}^{-1}$), up to a total fluence of $7.73 \times 10^{21}\text{ n.cm}^{-2}$ or $\sim 7\text{ dpa}$ ($E > 0.1\text{ MeV}$). The total time for the irradiation, and hence the duration at which the sample was at temperature, was 2456 hours.

Following tensile testing of the SS-J2 specimens (described elsewhere [2]), one half of the broken specimen was selected for polishing and mounting prior to focused ion beam (FIB) preparation of samples in ORNL’s Low Activation Materials Development and Analysis (LAMDA) Laboratory. [16] Needle-shaped samples to be used for atom probe tomography (APT) characterization were prepared using a FIB lift-out technique. [17] The APT samples were analysed in laser-mode with a Cameca Instruments LEAP 4000X HR instrument. The samples were analysed at 50 K, with a pulse frequency of 200 kHz, laser pulse energy of 50 pJ, and a detection rate of 0.005-0.02 atoms.pulse $^{-1}$. The atom probe data were reconstructed using Cameca’s Integrated Visualization and Analysis Software (IVAS) version 3.6.8. Standard parameters for the image compression factor (1.5), average evaporation field for the main constituent element ($\text{Fe} = 33\text{ V.mm}^{-1}$), and a detector efficiency of 0.36 were used. The bulk composition of the alloys were derived using the peak decomposition algorithm native to IVAS. [18, 19]

A sample of the Fe(18)CrAl alloy was selected for APT analysis in the as-received state to

Figure 1: Atom maps from the Fe(10)CrAl, Fe(15)CrAl, and Fe(18)CrAl specimens irradiated to 7 dpa. Only the Cr atoms are shown and the reconstruction thickness is 10 nm. Precipitation is clearly observed. The scale bar is 15 nm.

search for any pre-irradiation clustering of the Cr. No evidence of clustering was observed in neither atom maps, concentration isosurfaces, nor nearest neighbour distribution analysis. A χ^2 statistical analysis was performed to search for small-scale clustering, using a bin width of 50. The results were $\chi^2 = 70.2$ with 20 degrees of freedom. These values lead to a p -value of <0.00001 , meaning that there is no statistically relevant clustering of the Cr atoms occurring in the unirradiated sample (assuming a p -value cut-off of 0.05), and that the Cr is fully in solid solution. [13, 18]

Following neutron irradiation, all the alloys exhibited clustering of the Cr as shown in Figure 1. Clustering of this nature is indicative to the formation of α' within high Cr content ferritic alloys [11–13, 15] as a result of transitioning from the Fe-rich α phase, into the Cr-rich α' phase. [14] The presence of the α' is further confirmed through the use of a 30 at.% Cr concentration isosurface in the Fe(18)CrAl as shown in Figure 2. This demonstrates that the precipitates are highly enriched with Cr and that the precipitates are indeed α' , in agreement with previous studies on similar materials. [11, 12, 15]

The results presented in Figures 1 and 2 clearly show the formation of α' in all the alloys. However, what is less clear is the role of Al in the formation of the α' . In order to investigate the

Figure 2: Data reconstruction from the Fe(18)CrAl alloy irradiated to 7 dpa. α' precipitates are shown using a Cr concentration isosurface (30 at.%). The black dots are the Fe atoms (2% shown). The scale bar is 20 nm.

role of Al in α' precipitate formation, it is necessary to examine the clusters in more detail.

To obtain information about individual clusters, the maximum separation cluster search method was used, [18–20] utilizing the method described by Bachhev *et al.* to determine the search parameters d_{max} and N_{min} . [11] Although the bulk compositions can be relatively accurately derived using the peak decomposition algorithm¹ as discussed above, the IVAS software does not account for peak overlap in the time-of-flight (TOF) spectrum when using the maximum separation method. Peak decomposition in these material systems is critical due to the peak overlaps at 27 Da (mass-to-charge-state ratio) resulting from the field evaporation of $^{27}\text{Al}^+$, $^{54}\text{Cr}^{2+}$, and $^{54}\text{Fe}^{2+}$. At the time of data reconstruction, this peak must be ranged as a single element, which artificially enriches the apparent composition of the system in the element chosen, while depleting the apparent composition of the other two thereby giving an incorrect cluster composition. Without correcting for this overlap, the concentrations of the Al, Cr, and Fe would be incorrect. In order to apply this correction to the results of the cluster search algorithm and obtain accurate elemental concentrations, the relationship given in Equation 1 was used using the ion counts output from the maximum separation method, where X_{cor}^i is the corrected concentration for element X in cluster i , X_{bulk} is the bulk concentration of element X as given in Table 1, X_{total} is the total number of ranged ions of element X detected in the data set, N_{total} is the total number of ions of all species detected in the data set, X_{clus}^i is the number of ranged ions of element X detected in cluster i , and N_{clus} is the total number of ions from all species detected in cluster i .

$$X_{cor}^i = \frac{X_{bulk}}{\frac{X_{total}}{N_{total}}} \cdot \frac{X_{clus}^i}{N_{clus}} \quad (1)$$

The method to correct for cluster composition as described in Equation 1 was used in the characterization of the α' precipitates. Individual precipitate compositions for 200 spatially iso-

¹The term ‘relatively’ is used as IVAS uses the natural abundance of the constituent elements; however, neutron-irradiation induced transmutation results in an abundance that is skewed from the natural abundance thereby reducing the accuracy of the composition. However, this effect is minimal in the irradiation and material system described in this report.

Figure 3: Individual cluster compositions from 200 spatially isolated α' precipitates from the alloys (a) Fe(10)CrAl, and (b) Fe(18)CrAl.

lated α' precipitates from the Fe(10)CrAl and Fe(18)CrAl alloys are shown in Figure 3. For the Fe(10)CrAl alloys (Figure 3a), the α' precipitates are observed to primarily composed of Cr and Fe with a contribution of Al. A relatively large range of compositions is also seen, whereas the Fe(18)CrAl (Figure 3b) shows the primary components are Cr and Fe with a narrower compositional range of Al in relation to the Fe(10)CrAl alloy. Similar compositional variations were observed in the Fe(12)CrAl and Fe(15)CrAl alloys in that there was a primary concentration of Fe and Cr, with minor contribution of Al. The average cluster compositions for all alloys are given in Table 2, as are the matrix compositions (the composition of the material excluding the α' precipitates). From Table 2, it can be seen that as the Cr content of the base alloy increases, there is a decrease in the Fe from within the α' along with a decrease in Al, along with a commensurate increase in Cr content (within the standard deviations given).

Comparing the matrix and average cluster compositions in Table 2 with the results given in IVAS by separating out the clusters and the matrix and then performing the peak deconvolution shows a strong correlation between compositions - within errors induced by ion ranging. The strength of this new methodology is that corrected compositions for *individual* clusters can be determined with accuracy, rather than only the average cluster composition determination through IVAS. To test this further, the uncorrected average compositions were also determined and it was found that the average Al composition of the clusters was considerably elevated ($\sim 2-3$ at.%), and the Cr content diminished by ~ 4 at.%. This information is available in the supplementary materials.

The observed enrichment of Cr and depletion of Fe and Al from the α' clusters is also shown in the proximity histogram averaged over 5 spatially isolated, individual clusters shown in Figure 4. This general trend was observed in all the alloys examined, and in no cases was a core-shell nor a spherical exclusion volume deplete in Cr structure observed, but only a relatively discrete interface.

Looking in more detail at the composition of the clusters, it is clear that there is still some significant Al contained within the clusters, although this is below the bulk value indicating that partitioning of the Al has occurred. The partitioning factor for Al, k_{Al} , can be determined using the relationship $k_{Al} = [Al]_{\alpha} / [Al]_{\alpha'}$ [13] and is given in Table 2 for all the alloys. k_{Al} is approximately

the same for all alloys at ~ 1.65 , and when compared to α' formation in a recrystallized PM2000 alloy (bulk composition: 18.5 at.% Cr and 10.5 at.% Al; $k_{Al} = 1.3$) thermally aged at 475 °C over approximately the same time period [13] indicates that α' formation and Al rejection from the precipitates has occurred at an accelerated rate.

In the study of α' formation in model binary FeCr alloys, the Cr composition of the α' was found to be ~ 85 at.% following neutron irradiation to 1.82 dpa regardless of the initial composition of the alloy. [11] *It should be noted that variances exist between the Bachhav experiment and the one presented here including time at temperature (1328 hrs versus 2456, respectively), the irradiation dose (dpa), and the irradiation temperature.* In the FeCrAl alloys of interest in this study, the Cr content of the α' ranges from ~ 51 –63 at.% at neutron doses of 7 dpa, although the trend is not linear with bulk Cr content. This suggests that the Al is acting to suppress the maturation, i.e. retard the growth, of the α' precipitates and that even at 7 dpa, the α' may not be fully saturated although higher dose irradiations will be required to confirm this. This immaturity of the α' precipitates can be attributed to a change in the miscibility gap boundary of the phase diagram induced by the inclusion of Al into the system. [14]

The formation of immature, or unsaturated, α' precipitates has an implication on the mechanical property response. A previous study of the radiation response of irradiated FeCrAl alloys of the same composition applied the simplified dispersed barrier hardening (DBH) model to evaluate the contribution of the α' precipitates and dislocations to the irradiation-induced hardening response. [2] It was determined that the contribution of the α' precipitates to the hardening was an order of magnitude lower than that of the contribution by the dislocations ($a/\langle 100 \rangle$, $a/2\langle 111 \rangle$, and line dislocations). However, it is evident that further work is necessary to determine what is the underlying nature of the ‘softening’ of the α' precipitates: is there a lattice mismatch between the α' precipitates and the matrix, and is this different between the α' formed in FeCr and FeCrAl alloys; and to what extent does the Cr content within the α' have on dislocation mobility through the α' precipitates.

Statistics of the α' number density (n_p), volume fraction (f), and average radius are given in Table 3. *The precipitate radii, number densities, and volume fractions were calculated based on the number of ranged atoms determined through the cluster search algorithm, as described by Bachhav et al.* [11] Here there is a strong correlation between the alloy base composition and the α' number density and volume fraction, with both increasing with the alloys’ increasing Cr content. The average radius of the clusters is also given but there is no obvious trend here due to the large standard deviations. What can be derived from the information in Table 3 is that there are significantly fewer α' precipitates in the low Cr alloys – likely a result of the low Cr content not providing significant quantities of Cr to enable α' precipitation – and that they are approximately the same size. Comparing these values to those of FeCr binary alloys irradiated to 1.82 dpa [11], and several steel alloys irradiated up to 2.4 dpa at temperatures of 250, 325, and 400 °C [21] there are some clear differences, particularly with respect to the higher n_p and f (however, it should be noted that in [21] the small angle neutron scattering data were calculated based on the assumption that the α' precipitates had a composition of 95 at.% Cr, 5 at.% Fe – higher than the content determined through atom probe examination, and may result in artificially high n_p and f values). What is clear is that the addition of Al is altering the n_p , f , and the average radii when compared to irradiated binary alloys and conventional steels, and to fully elucidate the mechanisms underlying this modification of behavior, a further, more detailed study is required.

In summary, atom probe tomography has been used to characterize the α' precipitates formed in a range of FeCrAl alloys with varying Cr and Al content that have been neutron-irradiated to

Figure 4: Concentration-corrected proximity histogram averaged over 5 precipitate clusters from the Fe(18)CrAl sample. Depletion of the Al from the cluster is observed.

Table 2: Cluster analysis information as determined through atom probe tomography. Compositions are given in at.%. The compositional balance is made up of the minor solutes and impurities as listed in Table 1. The standard deviation of the cluster composition is given in parentheses. Also included is the Al partitioning factor (k_{Al}).

Alloy	Matrix composition			Average Cluster Composition			k_{Al}
	Fe	Cr	Al	Fe	Cr	Al	
Fe(10)CrAl	80.291	9.121	9.938	42.512 (6.819)	53.183 (7.897)	5.588 (1.896)	1.778
Fe(12)CrAl	80.209	10.428	8.748	44.389 (5.403)	51.147 (5.754)	5.240 (1.261)	1.669
Fe(15)CrAl	79.715	11.609	7.893	39.481 (6.035)	57.900 (5.837)	4.853 (1.251)	1.626
Fe(18)CrAl	79.804	12.847	6.525	34.095 (4.742)	62.531 (5.209)	3.866 (0.832)	1.688

Table 3: Cluster number densities (n_p), volume fractions (f), and average radius for each alloy. The standard deviation of the average radius is given in brackets.

Alloy	n_p ($\times 10^{24} \text{ m}^{-3}$)	f	Average Radius (nm)
Fe(10)CrAl	0.43	0.0211	1.681 (1.020)
Fe(12)CrAl	0.70	0.0366	1.849 (0.917)
Fe(15)CrAl	2.3	0.0727	1.662 (0.701)
Fe(18)CrAl	2.1	0.0961	1.972 (0.750)

a dose of 7 dpa at 320 °C. α' precipitates were found to have formed in all alloys, and the average Cr content of the α' was found to lie in the range of ~ 51 –63 at.% - a composition significantly lower than that of α' precipitates formed in irradiated FeCr binary alloys of similar Cr content, suggesting that the Al acts to perturb α' precipitation. It was also observed that partitioning of the Al occurred, with Al being rejected from the α' precipitates.

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20 nm

Figure 1

Fe(10)CrAl

Fe(12)CrAl

Fe(15)CrAl

Fe(18)CrAl

Figure 2

Figure 3a

Figure 3b

Figure 4