Microstructural changes in a neutron-irradiated Fe-15at.%Cr alloy

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Abstract

Microstructural changes in a Fe-15at.% Cr model alloy neutron irradiated to 1.82 dpa at 290°C were characterized by atom probe tomography. Homogenously distributed α' precipitates as well as fewer clusters containing Si, P, Ni, and Cr, were observed in the matrix. Grain boundary analyses before and after irradiation revealed segregation of Cr, with W-shape concentration profiles developing in the vicinity of grain boundary carbide and nitride particles. After irradiation, impurities such as C, Si and P were segregated to the grain boundaries. Zones depleted of α' clusters, and Si were found at the interfaces of carbide and nitride precipitates and along grain boundaries in the vicinity of these precipitates.

Keywords: Fe-Cr, neutron irradiation, atom probe tomography

1. Introduction

High chromium ferritic/martensitic (F-M) steels are one of the strong contenders for structural components of the next generation of nuclear reactors and future fusion reactors [1]. Under irradiation, F-M steels are much more swelling resistant than austenitic stainless steels and possess a balance of properties that make them attractive for such applications [2]. However, the long-term use of these steels in intense neutron irradiation environments requires reliable predictions of the evolution of their microstructures and mechanical properties. Developing accurate models that can predict phase transformations, accelerated diffusion, and other irradiation-affected phenomena, requires experimental insight and validation.

F-M steels, such as T91, HT-9 or HCM12A, typically contain 9-12 at.%Cr with small additions of Mo, V, W, Mn, Ni, C. The structural changes induced by irradiation, which have been extensively reported, are complex and include Ni and Si clustering [3-6], solute segregation to dislocations [6-9], grain boundary Cr segregation [3, 10-16] or Cr depletion [17-20]. Prior work on multicomponent steels, such as austenitic stainless steels and low alloy ferritic pressure vessel steels, has also revealed a sensitivity of the radiation response to small variations, not only in alloy solute contents, but also trace impurity concentrations [21, 22].

Focusing on grain boundaries, the evolution of their chemistry during irradiation is of particular importance because of its potential impact on mechanical properties and corrosion resistance. However, irradiation effects on chemistry, and more particularly on Cr concentration, at and near grain boundaries in ferritic Fe-Cr alloys is a highly debated issue in part because both Cr depletion and Cr enrichment at grain boundaries have been reported [23]. The origin of the opposing Cr enrichment versus depletion behavior has not yet been elucidated. Model Fe-Cr alloys have recently been the focus of a number of studies in an effort to better understand Cr behavior, eliminating the possible effects of other solutes, such as their interactions with point defects [24-28]. Grain boundary orientation was shown to be an important factor influencing Cr depletion in Fe-Cr alloys under ion [29] or Cr enrichment after neutron irradiation [16]. Temperature may also be an important parameter. The irradiation response of commercial FM steels under proton irradiation reveals Cr segregation at low temperature and Cr depletion above 600°C [30]. The alloy Cr concentration may be another factor impacting its redistribution under irradiation. Our recent study of the Fe 3-18Cr series after neutron irradiation, including the Fe-

15Cr alloy reported on here, showed that the phase boundary between the α phase (Cr solid solution in Fe) and the two-phase region $\alpha+\alpha'$, where α' is the Cr-rich phase, is close to 9 at. % at $\approx 290^\circ\text{C}$ [28]. Therefore, actual F-M steels, with higher Cr contents, could be subject to α' precipitation.

In an effort to systematically investigate the effect of Cr content, a series of model Fe-Cr alloys containing 3 to 18 at.%Cr were neutron irradiated in the Advanced Test Reactor (ATR) at the Idaho National Laboratory as part of the Department of Energy (DOE) sponsored ATR National Scientific Users Facility (NSUF) Program. The present article reports on pre- and post-irradiation microstructures of the supersaturated Fe-15Cr alloy forming α' precipitates during irradiation and also containing grain boundary carbides and nitrides particles. A companion article focuses on the changes occurring in an under-saturated Fe-6Cr alloy without α' precipitation or carbide or nitride phases at grain boundaries.

2. Materials and experimental methods

The Fe-15%Cr alloy used in this study was originally investigated by Gelles et al. in the 1980s as part of the fast breeder reactor program [31, 32]. A cold rolled sheet condition of this alloy was annealed under an argon atmosphere at 950°C for 15 minutes followed by air cooling, then re-annealed at 750°C for 1 h, again followed by air cooling. This resulted in an equiaxed and recovered structure with a relatively large grain sizes of order 50-100 μm , and a low dislocation density as indicted by low hardness values.

The Fe-15at.% Cr was irradiated in the ATR to a neutron fluence ($E>1\text{ MeV}$) of $1.1 \times 10^{21}\text{ n/cm}^2$ at $290 \pm 15^\circ\text{C}$ corresponding to a damage level of 1.82 displacements per atom (dpa). Nominal neutron flux and dpa rate are $2.3 \times 10^{14}\text{ n/cm}^2/\text{s}$ and $3.4 \times 10^{-7}\text{ dpa/s}$, respectively.

No microstructural differences are observed at the micron length scale between the as-received alloy and the neutron-irradiated alloy conditions. Electron back-scattered diffraction (EBSD) was used to identify grain boundaries with different orientations. APT specimen tips containing selected grain boundaries or matrix regions were prepared by a standard focused ion beam (FIB) milling procedure [33], using a Quanta 3D 200i dual beam SEM microscope. For the irradiated alloy, specimen preparation was performed at the Idaho Center for Advanced Energy Systems.

A LEAP 4000X HR instrument was used for atom probe tomography (APT) analyses. Specimens were cooled to a base temperature of 55K and analyzed in either voltage pulsing mode (with a pulse fraction of 20%) or laser mode (energy in the range of 30-60 pJ/pulse). The pulse repetition rate was set at 200 KHz, and a constant detection rate in the range of 0.003-0.005 atoms/pulse was used during data collection. Data reconstruction and analysis was performed using the Cameca Visualization and Analysis Software (IVAS 3.6.6). Standard parameters for the average evaporation field (33V/nm) and the detector efficiency (0.36) were used for reconstruction of the datasets. Information on tip geometry such as initial radius and shank angle used for the reconstruction was obtained from SEM images.

3. Results

3.1. Matrix

The alloy matrix compositions were determined from datasets obtained under identical voltage mode analysis conditions. The measured compositions for the as-received and neutron-irradiated conditions, provided in **Table 1**, are in good agreement with the nominal alloy Cr composition, but notably reveal the presence of trace impurities such as Ni, Si, P, and C.

Visual inspection of a reconstructed atom map of the pre-irradiated alloy shows a uniform three dimensional spatial distribution of Cr, as shown in **Fig. 1(a)**. Conversely, Cr-enriched clusters are observed in the neutron-irradiated condition. These are defined by a 34 at.%Cr iso-concentration surfaces, as illustrated in **Fig. 1(b)**. A proximity histogram based on this interface yields an average compositions of 87.2 ± 3.6 at.%Cr, which is consistent with the composition of the α' phase. The corresponding Cr content in the matrix (excluding α' precipitates) is 9.7 ± 0.6 at.%Cr. The number density and mean radius of the α' precipitates are estimated to be $(3.2 \pm 0.3) \times 10^{24} \text{ m}^{-3}$, and $1.3 \pm 0.2 \text{ nm}$, respectively. A detailed analysis of these α' clusters has been published elsewhere [28].

As shown in **Fig. 2(a)**, homogeneously distributed Si-P-Ni-Cr enriched clusters are also observed in the matrix after irradiation. An 0.8 at.% P threshold iso-concentration surface was used to define these clusters and estimate their compositions. A representative proximity histogram shown in **Fig. 2(b)** yields an average composition for the Si-P-Ni-Cr enriched clusters of 25.0

± 1.8 at.%Cr, 2.8 ± 1.8 at.% Si, 1.2 ± 0.4 at.% P, 4.7 ± 0.7 at.%Ni. The mean radius and number density of these clusters is estimated to be 2 ± 0.3 nm and $(5.4 \pm 0.4) \times 10^{22} \text{ m}^{-3}$, respectively. The latter is almost two orders of magnitude lower than that of the α' precipitates.

3.2. Grain boundary chemistry

The grain boundaries in both the pre- and post- irradiation conditions are decorated by a high density of chromium nitride and chromium carbide particles. The compositions of these phases are discussed in the next section and this section focuses on grain boundary chemistry away from such particles. The segregation behavior of solute atoms is known to be function of grain boundary orientation [16]. Thus boundaries with different misorientations are identified by EBSD mapping prior to specimen lift out. The concentration distribution profiles across grain boundaries are measured in thin axial slices along a 30 nm diameter cylinder oriented perpendicular to the boundary plane. The cylinder is carefully placed to avoid crystallographic poles and zone lines, which may contribute to APT composition artifacts. The Cr, Si, C, and P concentration profiles across a grain boundary with a misorientation angle greater than 15° in the as-received condition are shown in **Fig. 3**. The particular profiles were taken within 20 nm of a carbide particle present at the boundary.

Two particular grain boundary orientations ($\Sigma 5$ and a $\Sigma 3$) were selected for analysis in the post-irradiation condition. The $\Sigma 5$ grain boundary had a very dense distribution of precipitates, and the Cr concentration profile taken next to a carbide particle exhibits a “W” shape, as shown in **Fig. 4(a)**. Conversely, the $\Sigma 3$ grain boundary shows Cr segregation with an asymmetrical segregation profile across the grain boundary (**Fig. 5(a)**). The maximum to minimum Cr concentration ratio is highest for the $\Sigma 5$ boundary (with a W-profile) and lowest for the $\Sigma 3$ boundary; however these ratios are qualitatively similar. The behavior of Si, C, Ni, and P generally follow the Cr trends, i.e. W-shaped profiles at the $\Sigma 5$ grain boundary (**Fig. 4(b)**) and asymmetric segregation profiles at the $\Sigma 3$ grain boundary (**Fig. 5(b)**). However, the distribution of some elements in the as-received condition also appears to be asymmetric.

3.3. Grain boundary nitride and carbide precipitates

Chromium carbide and nitride precipitates are present at the grain boundaries in both the as-received and neutron-irradiated conditions. The compositions of the precipitates are summarized in **Table 2**. All possible mass spectra peak overlaps were taken into account and deconvoluted. The distribution profiles across the carbide and nitride particle interfaces in **Fig. 6** show comparable slight Cr depletion at the interphase boundaries. Following irradiation, the depletion is more pronounced with an average Cr concentration about 9 at.% Cr compared to 15% Cr in the adjoining regions and extends to a much larger width (~10-15 nm). The Cr depleted region around the particles is devoid of α' precipitates, as can be seen from 3-D reconstructed data in **Fig. 7**. Si and P also segregate at the carbide and nitride interfaces (not shown), again with a 15-20 nm wide depletion zone away from the interfaces. Additionally, the Cr concentration in both precipitate types is slightly increased in the irradiated condition.

As a side note, **Fig. 8** shows a comparison between the mass spectra from the carbide precipitate of irradiated (black colored) and as-received (red colored) sample. Boron (B) present in the carbide particle from a neutron irradiated sample is found to be mono-isotopic (^{11}B) whereas B from as-received condition is found in its natural isotopic distribution. The absence of ^{10}B in the irradiated condition is attributed to the transmutation reaction: $^{10}\text{B} + ^1_0\text{n} \rightarrow ^7_3\text{Li} + ^4_2\text{He}$. Since B is present in negligible quantity, it is unlikely to create any substantial population of He bubbles.

4. Discussion

A detailed study on α' precipitation for Fe-X Cr binary alloy series ($X = 3, 6, 9, 12, 15, 18$ at.%) is reported elsewhere [28]. The previous study showed that under irradiation, α' precipitation occurs in alloys containing Cr above the solubility limit (≈ 9 at.% Cr). The key mechanism appears to be accelerated precipitation at 290°C due to radiation enhanced Cr diffusion. The α - α' phase separation in the matrix contributes to hardening and embrittlement, e.g. [34, 35] and references therein.

There is a much lower density of Si-P-Ni-Cr enriched clusters, compared to the α' precipitates. The extremely low levels of Si, Ni and P in the alloy would seem to exclude a significant thermodynamic driving force for precipitation of the cited impurities, strongly suggesting a

radiation induced segregation (RIS) and radiation induced precipitation (RIP) mechanisms are operative in this case. Radiation-induced Si-P-Ni-Cr enriched clusters with comparable number densities and concentrations have previously been reported in lower Cr ferritic steels [36]. Notably, the impurity clusters are apparently not associated with extended irradiation-induced defects, like visible dislocation loops, and are independent of the α' precipitates. Thus the homogeneous distribution of the impurity clusters is somewhat puzzling, since RIS typically occurs at sinks for mobile point defects, such as loops, network dislocations and grain boundaries [37]. RIS is typically driven by persistent fluxes of defects to the sinks that couple differentially with solutes like Cr and Fe, such as in an inverse Kirkendall effect [38]. Under irradiation either vacancies or self-interstitials, or both, may be the mobile defect species responsible RIS [39]. In the present case, candidate sinks include small sub-nm vacancy cluster formed in cascades, and/or very small interstitial clusters (proto-loops). These defect clusters cannot be detected in the APT datasets and, in any event, could recover in-situ while leaving behind their solute remnants. Once formed the Si-P-Ni-Cr clusters could continue to grow by RIS, since mobile defects would either annihilate, or recombine, at their incoherent or coherent interfaces, respectively [40].

Understanding of the effects of irradiation on grain boundary chemistry in F-M is limited, as exemplified by previous observations of both segregation and depletion of Cr [23]. Further similar levels of enrichment occur with and without irradiation. In addition, the presence of carbides is known to affect grain boundary chemistry independently of irradiation. The Cr peaks in the as-received condition clearly show that segregation takes place thermally, during the processing time-temperature history. Enrichment of Cr at grain boundaries has been observed in austenitic stainless steels [41] and ferritic steels [46]. The Cr enrichment is presumably controlled by the temperature dependent combination of the segregation energy mediated thermodynamic partitioning to the boundary, and diffusion rates. This is qualitatively consistent with a ratio of 1.25 shown in **Fig. 3(a)**. Non-equilibrium thermal segregation (TNES) may occur as well, leading to Cr enrichment at grain boundaries due to the flow and annihilation of excess annealing temperature thermal vacancies [42, 43]. Balogh reported a Cr grain boundary thermal segregation energy of 2900 J/mole, which produces a McLean model peak Cr enrichment ratio of ≈ 1.2 at the heat treatment temperature of 750°C [44]. Additional segregation could occur during cooling. As noted above, TNES could also result in GB enrichment in the as-received condition.

In any event, some Cr boundary segregation is to be expected [45] in levels that are consistent with those observed.

We noted that thermal segregation is not unexpected, and that the magnitude of Cr enrichment levels is qualitatively similar between the as-received and neutron-irradiated alloys. The most obvious conclusion is that segregation at grain boundaries is not greatly affected by irradiation, possibly except for forming a W profile at the $\Sigma 5$ boundary. However, even this conclusion is confounded by the presence of boundary carbide and nitride phases, which take up Cr leading to local depletion as observed in the classical heat treatment sensitization effect [46]. The grain boundary precipitates may cause further depletion by consuming Cr in a way that may be promoted by radiation-enhanced diffusion. An absence of RIS would suggest that there is no bias associated with the diffusion of Cr by either interstitials or vacancies.

The W-shape profile has been observed in similar alloys after ion and neutron irradiation [15, 29]. W-profiles have been observed in some irradiated austenitic stainless steels with initial Cr segregation before irradiation [41, 47]. It has been hypothesized that these profiles are associated with an intermediate stage of irradiation induced Cr depletion near grain boundaries, that were initially thermally enriched, but are subsequently depleted, following a model developed by Nastar [48]. However it remains unclear as whether these could have also been affected by nearby carbide particles. On the other hand, no Cr-depleted zone is observed around the $\Sigma 3$ boundary. In the event of a RIS mechanism, it is expected that this interface would be less affected by irradiation due to its limited free volume and sink efficiency. That is, even if Cr diffusion is globally biased, this particular boundary may be more immune to RIS, as was previously observed under ion irradiation [29]. Further, the unsymmetrical profile of Cr shown in **Fig. 5(a)** might relate to the migration of the $\Sigma 3$ grain boundary under irradiation [49].

Systematic segregation Si, C and P at all interfaces is also observed (grain boundaries, carbide and nitride interfaces) with a depletion zone (10-20 nm wide), except for the $\Sigma 3$ boundary, which has no depletion zone. This might be interpreted to suggest that segregation of these impurities is due to RIS. However, it is well known that these elements, particularly C (that strengthens boundaries) and P (weakening boundaries causing temper embrittlement) very strongly thermally segregate to grain boundaries. Therefore, whether radiation-enhanced

diffusion (RED) and/or RIS operate for these elements and irradiation conditions remains inconclusive.

Additional observations using STEM to sample longer lengths of boundaries as a function of distance to the grain boundary particles, as well as observations after irradiation to larger dose will help clarify the mechanisms controlling the evolution of grain boundary chemistry. Annealing studies can also be used to separate thermal equilibrium from non-equilibrium RIS mechanisms.

5. Conclusions

The APT analysis of the microstructure in a Fe-15Cr alloys after neutron irradiation to 1.82 dpa at 290 °C revealed a high density $((3.2 \pm 0.3) \times 10^{24} \text{ m}^{-3})$ of α' precipitates formed by a radiation accelerated mechanism and a lower density $((5.4 \pm 0.4) \times 10^{22} \text{ m}^{-3})$ Si-P-Ni-Cr enriched clusters with no correlation with α' precipitates. Cr segregation was observed at grain boundaries both before and after irradiation. A W-shape profile developed at the boundaries near carbide particles while a corresponding Cr depletion zone occurs at Cr rich carbide and nitride interfaces. Si and P segregation at all interfaces is also associated with a Si/P depletion zone. The data reported here is not in itself conclusive, however it supports the conclusion that while segregation occurs in Fe-Cr alloys it is not greatly affected by irradiation and is more sensitive to the presence of grain boundary phases.

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Table 1: Chemical composition (in at. %) for as-received and neutron-irradiated samples measured with atom probe tomography.

	Cr	Si	P	Ni	Mn	V	C
As-received	14.8±0.3	0.06±0.02	0.003±0.001	0.05±0.02	0.03±0.01	0.002±0.001	0.02±0.01
Neutron-irradiated	15.1±0.4	0.04±0.02	0.02±0.01	0.02±0.01	0.02±0.01	0.01±0.005	0.02±0.01

Table 2: Chemical composition (in at. %) of carbide and nitride phases observed in as received and neutron irradiated samples measured with atom probe tomography.

		Cr	Fe	C	P, Si, Mn, V, Ni, B	
Carbide	As-received	59.2± 2.0	21±1.5	19.5±1.2	<0.1	
	Neutron-irradiated	61.8± 2.2	11.9±1.1	26±1.5	<0.1	
Nitride					N	P, Si, Mn, V, Ni, B
	As-received	68.6±2.5	2.7±0.5	6.4±1.1	22±1.4	<0.1
	Neutron-irradiated	71.3±3.1	2.2±0.5	6±0.9	20±1.8	<0.1

Figure 1. APT 3D reconstructions from regions away from grain boundaries in the (a) as-received condition (b) neutron irradiated condition. The Cr-enriched clusters are revealed by iso-concentration surfaces at 34 at.%Cr.

Figure 2. (a) 3D distribution of P, Ni, and Si atoms from the neutron irradiated condition. Encircled are clusters enriched in P, Si, and Ni. (b) Proxigram taken from clusters shown in (a). Insight is magnified part showing distributuin of Si, P, and Ni and table showing content of clusters.

Figure 3. (a) Cr and (b) minority elements segregation profiles across a large angle random grain boundary in the as-received condition.

Figure 4. (a) Cr and (b) C, Si, and P segregation profiles across a $\Sigma 5$ grain boundary. The dashed line in (a) indicates the extent of the α' depleted zone.

Figure 5. (a) Cr and (b) C, Si, and P segregation profiles across a $\Sigma 3$ grain boundary

Figure 6. Distribution profiles taken across (a) carbide and (b) nitride interfaces in the neutron-irradiated (dotted lines) and as-received (solid lines) conditions.

Figure 7. 3-D distribution of α' clusters (shown by iso-surfaces $\geq 34\text{at.}\%$) from the neutron-irradiated condition with (a) a nitride particle shown in green and (c) a carbide particle shown in brown.

Figure 8. Partial mass spectra from carbide particles in the as-received and neutron-irradiated conditions.