CORRELATIVE MICROSCOPY OF NEUTRON-IRRADIATED MATERIALS

Development of new, radiation-tolerant materials that maintain the structural integrity and safety margins over the course of a nuclear power reactor’s service life requires the ability to predict degradation phenomena.

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A nuclear reactor core is an incredibly demanding environment that presents several unique challenges for materials performance. Materials in modern light water reactor (LWR) cores must survive several decades in high-temperature (300-350°C) aqueous corrosion conditions while being subject to large amounts of high-energy neutron irradiation. Next-generation reactor designs seek to use more corrosive coolants (e.g., molten salts) and even greater temperatures and neutron doses. The high amounts of disorder and unique crystallographic defects and micro-chemical segregation effects induced by radiation inevitably lead to property degradation of materials. Maintaining structural integrity and safety margins over the course of the reactor’s service life thus necessitates the ability to understand and predict these degradation phenomena in order to develop new, radiation-tolerant materials that can maintain the required performance in these extreme conditions.

Historically, performing the neutron radiation damage characterization necessary to assess radiation tolerance and performance has faced two primary challenges. First, preventing undue radiation exposure and contamination is problematic, as neutron absorption tends to generate radioactive isotopes in a material, which can make materials handling hazardous without specialized equipment and facilities. As such, the required sample preparation for post-irradiation examination (PIE) often needs to be performed in shielded hot cells and is limited to functions that can be performed therein. Practically speaking, this often precludes access to advanced microstructural characterization tools such as transmission electron microscopes (TEMs) and makes even basic characterization procedures much more costly. Second, neutron irradiation experiments typically have a long turnaround time, as achieving the doses necessary to produce end-of-life microstructure and mechanical properties in a material requires that specimens be exposed in a commercial reactor core for a length of time equivalent to the expected service lifetime. As a result, researchers in this field often use high-energy ion beam accelerators in attempts to emulate neutron damage processes at a much faster rate without inducing radioactivity in specimens. Although these methods provide valuable insight into a material’s irradiation response, they are not completely predictive due to differences in the mechanism in which charged particles and neutrons impair energy to the crystal structure[1].

Fortunately, modern PIE experiments can make use of specialized high-flux test reactors and dedicated characterization facilities in order to circumvent some of these issues. The Advanced Test Reactor (ATR) at Idaho National Laboratory (INL) and the High Flux Isotope Reactor (HFIR) at Oak Ridge National Laboratory (ORNL) are examples of two specialized nuclear reactor designs in the U.S. capable of inducing neutron damage structures at much greater rates compared to commercial LWRs. Further, access to dedicated, radiation-friendly characterization laboratories available through user facilities such as the Nuclear Science User Facilities (NSUF, atmnsuf.inl.gov) can provide the resources and personnel necessary to limit occupational exposure and prevent the spread of radioactive contamination.

An important tool within these user facilities and radiological characterization laboratories is the focused ion beam (FIB), used to prepare specimens for both TEM and atom probe tomography (APT) characterization. Sample preparation through FIB techniques has been particularly impactful in working with radioactive materials due to the significantly smaller working sample volumes leading to increased scientific yield gained from individual experiments. Using carefully performed FIB lift-out techniques, a highly radioactive bulk specimen can be reduced to such a minute volume that it no longer poses a significant exposure risk. As even a single bulk sample can have significant associated cost after irradiation in a reactor like HFIR, extracting the maximum amount of information from these samples is crucially important. As FIB can produce targeted, site-specific analysis and allows for multiple TEM and APT specimens to be prepared from a single bulk sample, it is extremely useful for maximizing the scientific and monetary value of a single bulk irradiated sample.

Some examples of radiation-induced microstructural defects being studied using these techniques include dislocation loops, cavities, segregation, and precipitates. Characterization of these nanoscale features necessitates advanced microscopy equipment and techniques that often require special considerations when performing data collection or analysis for radioactive materials. This article illustrates the use of these advanced techniques to characterize precipitates in neutron-irradiated Fe-Cr-Al alloys at ORNL, which have extensively utilized the aforementioned research reactors and user facility characterization laboratories. However, the techniques described here can be readily extended to other materials as well.

**CHARACTERIZATION OF IRRADIATED Fe-Cr-Al**

Fe-Cr-Al alloys are being considered as a possible replacement for Zr-based fuel cladding materials currently used in commercial LWRs for increasing safety margins and enhancing accident tolerance as part of the DOE’s Advanced Fuels Campaign[2]. Similar to other high-Cr ferritic alloys, Fe-Cr-Al alloys have excellent high-temperature aqueous corrosion and radiation-induced swelling resistance[3], but are susceptible to radiation-induced hardening and embrittlement due to the precipitation of nanoscale Cr-rich α’ phase precipitate particles at temperatures below 475°C. Though the kinetics for formation of this phase at LWR-relevant temperatures are slow, this process has been shown to be accelerated by neutron-induced radiation damage[4]. An understanding of how the formation of this phase is affected by composition and how the precipitate microstructure evolves with radiation dose is essential in order to mitigate the embrittlement response in
designing a nuclear-grade Fe-Cr-Al alloy for LWR cladding applications.

To this end, neutron irradiation and PIE analysis studies were performed on four Fe-Cr-Al model alloys with nominal compositions ranging from 10-18 wt% Cr and 2.9-4.8 wt% Al. Alloy compositions, as determined by inductively coupled plasma optical emission spectroscopy (ICP-OES), are shown in Table 1. These materials were machined into SS-J2 sub-sized tensile specimens and irradiated in HFIR to various nominal damage doses up to 13.8 displacements per atom (dpa) at a target temperature of 320°C, corresponding to a maximum exposure time of approximately 4900 hrs. Dpa commonly describes radiation damage and is defined as the average number of times an atom is displaced from a lattice site for a given fluence of energetic particles. Dpa is calculated based on the fluence and energy spectrum of incident particles for a given material. The specimens in the 13.8 dpa condition are expected to provide a reasonable approximation of material properties and microstructure at the end of the typical LWR fuel cladding lifetime. Details of final irradiation conditions are shown in Table 2.

Following irradiation, an assessment of tensile behavior was performed using room temperature and elevated temperature tensile testing with subsequent scanning electron microscopy (SEM) fracture surface analysis in-cell at the Irradiated Materials Examination and Testing (IMET) Hot Cell Facility at ORNL. Fractographs for a low- and high-dose condition of the Fe-18Cr-2.9Al following room temperature tensile tests demonstrate clear differences in specimen failure mode (Fig. 1a-b), with typical dimple ductile fracture observed at early-life doses transitioning to brittle, transgranular cleavage fracture at end-of-life doses. Tensile tests performed at 320°C after irradiation demonstrated ductile failure mechanisms in all dose conditions studied (Fig. 1c-d).

Broken half-tensile heads from each material condition were then prepared, packaged for on-road shipping, and shipped to the general purpose small-angle neutron scattering (SANS) beamline at ORNL for diffraction-based analysis of nanoscale η' precipitates in the microstructure. SANS is a non-destructive analysis technique in which an incident beam of neutrons is elastically scattered by interactions with nuclei or with the magnetic moment of unpaired electrons. Bulk samples used here (volume ~8 mm³) pose a significant radiological threat, so special care is taken during SANS investigations to minimize user interaction. These larger specimens are necessary in order to fit the 4-mm-diameter aperture sizes and allow for sufficient scattering to maintain an adequate signal-to-noise ratio in the SANS data. Two dimensional diffractograms were collected at room temperature at three different detector configurations. An example of

**TABLE 1 — Fe-Cr-Al MODEL ALLOY COMPOSITIONS INVESTIGATED IN THIS RESEARCH**

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Fe (%)</th>
<th>Cr (%)</th>
<th>Al (%)</th>
<th>Y (%)</th>
<th>C (%)</th>
<th>Si (%)</th>
</tr>
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<tbody>
<tr>
<td>Fe-10Cr-4.8Al</td>
<td>10.01</td>
<td>4.78</td>
<td>0.038</td>
<td>0.005</td>
<td>&lt;0.01</td>
<td></td>
</tr>
<tr>
<td>Fe-12Cr-4.2Al</td>
<td>11.96</td>
<td>4.22</td>
<td>0.027</td>
<td>0.005</td>
<td>0.01</td>
<td></td>
</tr>
<tr>
<td>Fe-15Cr-3.9Al</td>
<td>15.03</td>
<td>3.92</td>
<td>0.035</td>
<td>0.005</td>
<td>0.01</td>
<td></td>
</tr>
<tr>
<td>Fe-18Cr-2.9Al</td>
<td>17.51</td>
<td>2.93</td>
<td>0.017</td>
<td>0.005</td>
<td>&lt;0.01</td>
<td></td>
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*S, O, N, and P contents at or below 10 ppm.

**TABLE 2 — SUMMARY OF Fe-Cr-Al ALLOY CAPSULE IRRADIATION CONDITIONS**

<table>
<thead>
<tr>
<th>Capsule ID</th>
<th>Exposure time (hours)</th>
<th>Neutron flux (n/cm²s) E &gt; 0.1 MeV</th>
<th>Neutron fluence (n/cm²) E &gt; 0.1 MeV</th>
<th>Dose rate (dps/s)</th>
<th>Dose (dpa)</th>
<th>Irradiation temperature (°C)</th>
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<tr>
<td>FCAY-01</td>
<td>120</td>
<td>8.54 x 10¹⁴</td>
<td>3.69 x 10²⁰</td>
<td>7.7 x 10⁻⁷</td>
<td>0.3</td>
<td>334.5 ± 0.6</td>
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<tr>
<td>FCAY-02</td>
<td>301</td>
<td>8.54 x 10¹⁴</td>
<td>9.25 x 10²⁰</td>
<td>7.7 x 10⁻⁷</td>
<td>0.8</td>
<td>355.1 ± 3.4</td>
</tr>
<tr>
<td>FCAY-03</td>
<td>614</td>
<td>8.84 x 10¹⁴</td>
<td>1.95 x 10²¹</td>
<td>8.1 x 10⁻⁷</td>
<td>1.8</td>
<td>381.9 ± 5.4</td>
</tr>
<tr>
<td>FCAY-04</td>
<td>2456</td>
<td>8.74 x 10¹⁴</td>
<td>7.73 x 10²¹</td>
<td>7.9 x 10⁻⁷</td>
<td>7.0</td>
<td>319.9 ± 12.7</td>
</tr>
<tr>
<td>FCAY-05</td>
<td>4914</td>
<td>8.74 x 10¹⁴</td>
<td>1.55 x 10²²</td>
<td>7.8 x 10⁻⁷</td>
<td>13.8</td>
<td>340.5 ± 25.7</td>
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</table>

Fig. 1 — Comparison of fracture surfaces for Fe-18Cr-2.9Al alloy irradiated to 1.8 dpa (early life) and 13.8 dpa (near end-of-life) conditions.
Fig. 2 — (a) Raw SANS diffractogram for Fe-18Cr-2.9Al alloy, irradiated to 13.8 dpa at 341°C. (b) Final SANS scattering intensity curve, combining data from three distinct detector configurations, and example fit of analytical model to the data.

Fig. 3 — SEM micrographs of representative Fe-Cr-Al specimens prepared for (a) APT analysis, and (b) TEM and STEM analysis.

Fig. 4 — Atom probe reconstruction showing precipitate microstructure in Fe-15Cr-3.9Al alloy, irradiated to 7 dpa at 320°C. Precipitates are displayed using 34 at.% Cr concentration isosurfaces (purple) with 2% of total matrix Fe atoms shown (black).

A diffractogram for the Fe-18Cr-2.9Al specimen irradiated to 13.8 dpa at 340°C is shown in Fig. 2a, in which the precipitate signal manifests as a red-orange contrast ring around the central zero-beam (black contrast). Radial reduction of these diffractograms to one-dimensional curves allows analytical models to be fit to the data, from which bulk-averaged precipitate morphology information can be extracted (Fig. 2b).

Sections from the remaining half-tensile specimens opposite the strained neck were cut using a low-speed saw in the hot cells and shipped to the Low Activation Materials Development & Analysis (LAMDA) facility at ORNL for FIB sample preparation. LAMDA is a specialized facility designed for state-of-the-art characterization of low-radiological threat fuel and metallic specimens. Much less material is required for FIB sample preparation and subsequent analyses compared to SANS, and the volume reduction in the hot cell was sufficient to allow for out-of-cell hand polishing of specimens in LAMDA using standard metallographic techniques with appropriate personal protective equipment (PPE) and dosimetry. Polished specimens were then installed in a remotely-operated FEI Quanta 3D Dual-Beam FIB that is housed in a lead-lined room in order to shield personnel from radiation exposure. Operators of FIB equipment are specially trained to handle the radiological samples and a focus is placed on efficient loading practices to minimize exposure to the radioactive specimens. Standard lift-out techniques were then used to prepare microtip needles for APT analyses and lamellae for scanning transmission electron microscopy (STEM) investigations, examples of which are shown in Fig. 3.

APT investigations allowed for an atomic-scale study of individual precipitate composition and morphology within a very small analysis volume. Data collection was performed using the Cameca Instruments Local Electrode Atom Probe (LEAP) 4000X HR at either the Center for Nanophase Materials Sciences (CNMS) at ORNL or at the Center for Advanced Energy Studies (CAES) at INL. Both facilities are capable of handling radiological samples, but the significant volume reduction (< 100 μm³ on a single APT microtip coupon) promotes ease of handling when working at these laboratories. A representative reconstruction of a Fe-15Cr-3.9Al specimen irradiated to 7 dpa at 320°C is shown in Fig. 4. APT results reveal that Al additions appear to reduce the Cr content of precipitates when compared to binary Fe-Cr alloys, and the observed precipitate morphology trends are in agreement with those seen in the SANS study, validating the
models used in the scattering analysis. Artifacts of nuclear transmutation resulting from neutron absorption are observed in the generated time-of-flight spectrum as manifested by peak ratios that are inconsistent with expected natural isotopic abundances of constituent elements. In addition, peaks corresponding to transmutation products, such as V and Mn, are also identified.

Due to the semi-coherency of α’ particles in an α-ferrite matrix, conventional diffraction contrast-based TEM techniques are not useful for studying the Cr-rich precipitates in this system, necessitating the use of chemically sensitive electron microscopy techniques[9]. As such, energy dispersive x-ray spectroscopy (EDS) was coupled with STEM to acquire spectral images of the precipitate microstructure. STEM/EDS data collection was performed on the FEI Talos F200X S/TEM located in the LAMDA facility. Due to the high efficiency of the FEI Talos system, care must be taken when performing data analysis as the energetic emissions of radioactive decay from irradiated samples can be easily detected along with the characteristic x-rays, potentially muddling the observed x-ray spectrum; this effect is significantly reduced with FIB prepared specimens over more traditional 3 mm disc specimens. The x-ray maps were collected concurrently with annular dark field (ADF) images on the [111] zone axis, allowing for simultaneous imaging of dislocation loops[10] and collection of EDS spectra in these materials. Figure 5 demonstrates that α’ precipitates appear to nucleate homogenously in the bulk material, with no bias for dislocation loop or other defect sites.

THE FUTURE OF NUCLEAR MATERIALS RESEARCH

Modern nuclear materials characterization capabilities allow for an in-depth, multifaceted investigation of nanoscale precipitation events in alloys, as demonstrated for α’ phase precipitation in neutron-irradiated Fe-Cr-Al alloys for accident-tolerant nuclear fuels applications. The resulting detailed analysis of the mechanisms and dependencies of precipitation in this system has informed design decisions within the Fe-Cr-Al alloy development program of the DOE’s Advanced Fuels Campaign. Generation II Fe-Cr-Al engineering alloys with down-selected compositions based on this work are currently undergoing irradiation in HFIR to study the effect of minor alloying element additions on alloy radiation tolerance with the goal of recommending a nuclear-grade Fe-Cr-Al LWR cladding material in the near future.

Fe-Cr-Al alloys are just one of many material systems currently being developed for nuclear applications. For example, SiC is being extensively investigated as an alternative LWR cladding material and for advanced TRISO particle fuel for gas-cooled reactor technologies. Late-blooming phases (LBP) that may embrittle reactor pressure vessel (RPV) materials are also under investigation in order to extend commercial LWR operating licenses from 60 to 80 years. Additionally, improved radiation tolerance of oxide-dispersion strengthened (ODS) and nanostructured materials is being explored for other in-core components.

Advancing nuclear materials technology and developing robust radiation-tolerant alloys, ceramics, and nuclear fuels is critical for both maintaining and improving the existing commercial LWR technologies in addition to enabling the construction of next-generation reactor designs with even more demanding environments for materials performance. The modern characterization capabilities discussed here have greatly facilitated high-quality characterization research on nanoscale radiation effects in materials. The continued adoption of advanced characterization techniques and equipment in addition to ample access to this equipment by nuclear materials researchers is anticipated to play a central role in enabling informsd materials development for nuclear applications.

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References