Response of nanostructured ferritic alloys to high-dose heavy ion irradiation ☆

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ABSTRACT

A latest-generation aberration-corrected scanning/transmission electron microscope (STEM) is used to study heavy-ion-irradiated nanostructured ferritic alloys (NFAs). Results are presented for STEM X-ray mapping of NFA 14YWT irradiated with 10 MeV Pt to 16 or 160 dpa at −100 °C and 750 °C, as well as pre-irradiation reference material. Irradiation at −100 °C results in ballistic destruction of the beneficial microstructural features present in the pre-irradiated reference material, such as Ti–Y–O nanoclusters (NCs) and grain boundary (GB) segregation. Irradiation at 750 °C retains these beneficial features, but indicates some coarsening of the NCs, diffusion of Al to the NCs, and a reduction of the Cr–W GB segregation (or solute excess) content. Ion irradiation combined with the latest-generation STEM hardware allows for rapid screening of fusion candidate materials and improved understanding of irradiation-induced microstructural changes in NFAs.

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1. Introduction

Development of new materials is the primary obstacle to the deployment of Generation IV (GenIV) fission power technologies [1–6] and among the major obstacles to fusion power [7,8]. Many materials considered candidates for fission are also likely candidates for fusion systems [9]. These new reactor systems, fission or fusion, will require materials that can withstand radiation doses of several hundred dpa (displacements per atom) over years or decades of service, at temperatures of several hundred degrees Celsius, while exposed to corrosive coolants such as supercritical water or liquid metal [7].

Understanding the response of microstructures to these enormous levels of radiation damage (100 dpa and above) is necessary to select suitable candidate materials for advanced reactor systems. However, test reactors typically apply relatively low rates of damage (typical ranges are 10^{-8} to 10^{-6} dpa/s, or ≈0.3–30 dpa/year) [10–13]. For example, producing a damage level of 500 dpa by neutron irradiation would require decades in a test reactor, and would result in prohibitive levels of activation and consequent induced radioactivity in the specimen [14]. Therefore, ion irradiations are a better alternative to simulate high-dose neutron irradiations in much shorter time periods and without the significant induced radioactivity. Proton irradiation may be used to apply dose rates ~10^{-5} to 10^{-3} dpa/s [12,15,16], and heavy ions, such as Ni, Au, Pt, or self-ions, may be used to apply rates of 10^{-3} to 10^{-1} dpa/s [12,16,17], or ~100–1000 dpa/day. As a result, heavy ion irradiation is an excellent means for the rapid screening of candidate alloys for high-dose applications. The primary disadvantages to heavy ion irradiations are the relatively shallow damage depths resulting from the high stopping power of the ions; commonly 2000 nm or less [12,13,18]. Additionally, there is a gradient of damage with depth, which results in rapid changes of dose as a function of depth into the material. The irradiating species also changes the local elemental composition of the material, which is particularly noticeable when a non-self-ion is used.

In ultrafine structured materials, such as nanostructured ferritic alloy (NFA) 14YWT [19], where grains sizes range between 20 and 400 nm, grain boundaries are enriched with multiple solutes. Several nanocluster (NC) and precipitate populations with sizes of ~1 nm, ~5 nm, and ~50 nm are present. Scanning electron microscopy (SEM) can image the fine grain size and the large to medium precipitates, but is able to image or compositionally map neither NCs nor grain boundary segregation. Atom probe tomography (APT) and scanning/transmission electron microscopy (S/TEM) can detect all of the features but generally lack the analytical field-of-view to examine the entire depth of typical heavy ion implants [17,20].

The latest generation aberration-corrected STEM instruments fitted with large-solid-angle X-ray energy dispersive spectroscopy

(EDS) detectors, however, allow such rapid imaging and elemental mapping over large areas *as to make possible the interrogation of an entire heavy ion implantation profile*, from surface through the damage peak to beyond the zero-dpa damage tail. This advance allows comprehensive "one-map" analysis of the radiation response of the material at a given irradiation temperature. By mapping a matrix of temperatures and fluences (proportional to peak doses), a comprehensive understanding of the material's radiation response can be obtained.

Because of the ability of a modern aberration-corrected, high-collection-efficiency STEM to map elemental distributions at nanometer or sub-nanometer resolution, the same specimens and instrument used to map the broad response of the entire heavy ion implant can also be used to map small regions and determine the qualitative distribution of elements, for instance, between different individual NCs, precipitates, and grain boundaries, which complements the single-atom (but smaller field-of-view) capabilities of APT.

In this paper, we examine a 14YWT NFA irradiated by Pt at series of different temperatures. The constituent distribution is mapped using an FEI Titan instrument with ChemiSTEM technology. Approximately 500 nm × 2000 nm EDS maps are presented, *which contain the entire in-depth distribution of the heavy ion response for each tested temperature*, describing the material's irradiation response at a glance. Additional high-resolution maps showing individual NCs and grain boundaries help describe differences in these features arising from irradiation dose and temperature, complementing APT studies.

2. Materials and methods

2.1. NFA fabrication and irradiation

This study used a 14YWT nanostructured ferritic alloy (NFA), with the nominal composition shown in Table 1. The material was produced by mechanically alloying together the Fe–Cr–W–Ti powder with Y_2O_3 powder, and then canning and extruding the resulting flakes at 850 °C. Polished bar-shaped specimens were irradiated with 10 MeV Pt^{3+} ions at either −100 °C or 750 °C to a maximum fluence of 4×10^{20} Pt/m^2, in the 3.0 MeV tandem accelerator facilities within the Environmental Molecular Sciences Laboratory (EMSL) at the Pacific Northwest National Laboratory (PNNL). The ion beam was rastered over the sample surface with a Pt ion flux of $\sim 2 \times 10^{16}$ Pt/m^2-sec, corresponding to an average damage dose rate of $\sim 10^{-2}$ dpa/s at the damage peak at a depth of ~ 800–900 nm.

Calculations under "full cascades," using the equations recommended by the Stopping and Range of Ions in Matter (SRIM) software manual [21] used by previous studies in our group [17,19,20,22–24], indicate peak doses of ~ 30 and ~ 300 dpa for these particular implants. However, a recent paper [25], drawing on past works [26–29], recommends a different method of converting SRIM simulations into dpa. Calculating 10 MeV Pt incident onto $Fe_{85}Cr_{14}W_1$ of density 7.8 g/cm³ (8.3×10^{22} atoms/cm³), under Kinchin–Pease mode, with 40 eV displacement energy and 0 eV

lattice binding energy, 10^5 ions simulated, peak doses of ~ 16 and ~ 160 dpa are obtained from the recommended method. No SRIM simulation will be "correct" in the sense of agreeing with the number of surviving Frenkle pairs calculated by molecular dynamics [30], but here we use the proposed standardized method of Stoller et al. [25] rather than the SRIM "displacements = vacancies + replacement collisions" full-cascade calculation [21] to be consistent with what will no doubt become future practice. The samples examined are summarized in Table 2. A bright field (BF) STEM image along with SRIM simulation parameters for 4×10^{20} Pt/m^2 fluence is presented in Fig. 1. The energy loss panel in Fig. 1 uses the terminology of Stoller et al.: "ionization" is energy lost to electronic excitations (SRIM output file IONIZ.TXT) and "phonon" is energy lost to target atoms (SRIM output file PHONON.TXT). Summing the integrals of these curves yields the incident beam energy.

2.2. Sample preparation and pre-screening

TEM/STEM thin foil samples were prepared from the as-implanted surfaces in a FIB–SEM (focused ion beam-scanning electron microscope) instrument. In situ liftout sections were prepared, and thin regions that were >2 μm deep and 2–5 μm wide were milled into the liftouts. Final FIB milling and polishing was accomplished with 5 keV Ga^+ ions, along with simultaneous imaging under 20 keV electrons with a bright field transmission detector.

Samples were pre-screened by imaging in a 200 keV field-emission TEM/STEM (Philips/FEI CM200FEG) instrument. Low-magnification energy-filtered TEM (EFTEM) thickness maps indicated FIB-prepared specimen thicknesses in the ion-implanted areas of interest were ~ 0.3–0.6 t/λ, for thickness t and electron mean free path λ. In EFTEM at 200 keV, λ is estimated as 100–150 nm [31], so t is estimated at ~ 30–90 nm over most of the specimen areas.

2.3. Aberration-corrected electron microscopy

A probe-corrected FEI Titan G2 instrument with ChemiSTEM technology [32] was used for X-ray mapping experiments, operated in STEM mode at 200 keV with a probe current maintained at 5.5–7.0 nA and an estimated probe size of ~ 0.5 nm. Besides all the advantages inherent to probe correction for EDS studies [33], this instrument was equipped with a large-area, 4-chip silicon drift detector (SDD) system [34,35] with solid angle of collection ~ 0.7 sRad. These large-area detectors are highly advantageous because extremely low levels of solute can be detected [34], in part due to the higher signal/background ratio inherent to EDS in comparison to other techniques such as EELS [36]. Single-atomic-column EDS mapping has been demonstrated previously [37].

The FIB-thinned lamella specimens were attached to 3-mm-diameter molybdenum half-disk grids. The grids were rotated to shadow only one of the four SDD detectors, where the grid-shadowed detector was not used. All maps and count rates are thus from three of the four detector quadrants. Depending on local

Table 1
Material bulk composition.

Element	Fe	Cr	Y	W	Ti	O	C	Si	N
at.%	Bal.	13.93	0.14	0.16	0.24	0.39	0.24	0.16	0.15
wt.%	85.41	13.13	0.22	0.54	0.19	1140 ppm	530 ppm	0.08	385 ppm
	Al	Mn	Ni	P	Mo	Nb	Cu	B	S
at.%	0.04	0.04	0.028	0.008	0.006	0.006	0.001	Trace	Trace
wt.%	0.02	0.04	0.03	0.004	0.01	0.01	0.01	8 ppm	0.003