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ORIGINAL REPORT

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Beam-contamination-induced compositional alteration and its neutron-atypical consequences in ion simulation of neutron-induced void swelling

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ABSTRACT

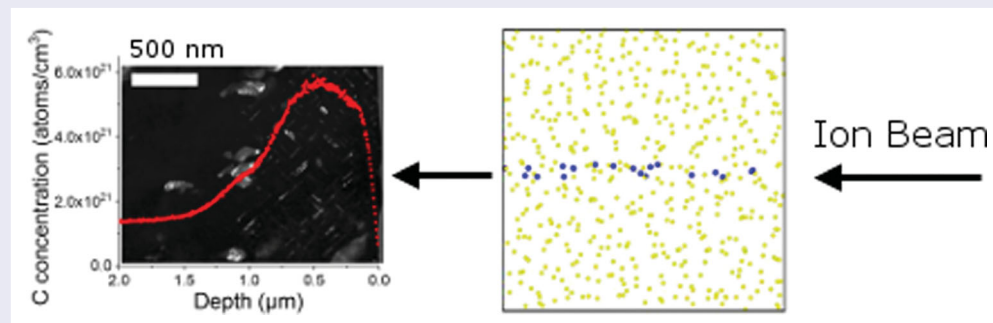
Although accelerator-based ion irradiation has been widely accepted to simulate neutron damage, neutron-atypical features need to be carefully investigated. In this study, we have shown that Coulomb force drag by ion beams can introduce significant amounts of carbon, nitrogen, and oxygen into target materials even under ultra-high vacuum conditions. The resulting compositional and microstructural changes dramatically suppress void swelling. By applying a beam-filtering technique, introduction of vacuum contaminants is greatly minimized and the true swelling resistance of the alloys is revealed and matches neutron behavior closely. These findings are a significant step toward developing standardized procedures for emulating neutron damage.

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KEYWORDS

Ion-beam processing; ion implantation; precipitation



IMPACT STATEMENT

An innovative 'beam shaking' technique is proposed to reduce beam-induced impurity contamination in accelerator-based ion irradiation. Without this technique, void swelling of ion-irradiated alloys can be greatly underestimated.

Introduction

Currently, the use of austenitic steels as fuel cladding in fast reactors has been limited to doses below ~ 150 dpa due to void swelling exceeding $\sim 10\%$, a condition that induces severe embrittlement [1,2]. As a consequence, fuel burn-up is limited to ~ 10 – 12% rather than the desired limit of $\sim 30\%$. To extend the cladding lifetime and thereby the attainable burn-up, there has been a move to replace austenitic steels with ferritic/martensitic (F/M) alloys or their oxide-dispersion-strengthened variants that have been observed to swell less than their austenitic counterparts [3,4]. Examples of reactors using this approach include BN-600 (Russia), the recently constructed BN-800 (Russia), and the PHENIX and SUPER-PHENIX (France) [5].

Previous studies have shown that ion irradiation can achieve steady-state swelling rates identical to those observed in neutron irradiation in both austenitic and F/M steels [6,7]. However, the limited range of the bombarding ions and strong internal dpa rate gradients along the ion path give rise to a variety of neutron-atypical effects [8–11]. Of these, an important neutron-atypical phenomenon involves compositional alteration along the ion path [12–14]. Furthermore, surface preparation becomes increasingly important for ion irradiation to ensure the near-surface region is reasonably free of defects and contaminants.

Contaminant molecules in an accelerator system can be ionized and entrained into the beam by Coulomb drag

effects, implanting onto the ion-irradiated area. These are typically H_2O , N_2 , CO , CO_2 , and heavier hydrocarbons. The entrainment occurs along the entire beam line, regardless of whether the beamline or target chamber is under high vacuum (e.g. $< 10^{-7}$ torr) or not. Among various contaminating elements, carbon is the most crucial since carbon is known to strongly influence microstructural evolution and swelling in both austenitic and ferritic alloys [1,4].

In the current study, HT9, an F/M alloy, was selected due to its reported low void swelling [15–17]. Ion irradiation was performed both with and without a filtering system to evaluate the impact on both composition and microstructural evolution. The present study is important to establishing a standard procedure or set of best practices which impact a wide range of ion beam modification, characterization, and irradiation studies.

Experimental procedure

HT9 specimens with composition given in Table 1 were annealed at 1040°C for 30 min and air cooled. They were tempered at 760°C for 1 h, followed by air cooling. Specimens were mechanically polished to 4000 grit SiC paper and jet electropolished using a solution of 5 vol.% perchloric acid and 95 vol.% methanol at -40°C and 20V.

Ion irradiation was performed using 3.5 MeV Fe^{2+} ions. A defocused ion beam was utilized to produce a static beam with a 10–15% variation in uniformity across the beam and a time-averaged peak dpa rate of 1.74×10^{-3} dpa/s maintained within $\pm 5\%$ over the duration of the irradiation [9,18]. Specimens were fixed to the stage using a carbon-free silver paste (Ted Pella, Inc. Product #16047).

Two sets of ion irradiation were conducted. The first set of specimens were irradiated to doses of 200, 400, and 600 dpa at the peak (herein referred to as 200, 400, and 600 dpa) at 450°C and did not utilize the ion beam filtering technique. The second set utilized a filtering system and achieved doses of 200, 600, and 800 dpa at 450°C . The filtering system comprised three deflection magnets spaced ~ 1.1 m apart along the beamline, with the last magnet 1.1 m from the target specimen. A static magnetic field was selected such that the deflection angle for the ion was approximately 2° for the first and last magnetic deflectors, and -4° for the second. Liquid nitrogen cold

traps were placed in the beamline ~ 0.7 m from the target chamber and on the chamber. All doses were calculated using the Kinchin-Pease option of the SRIM-2013 code with a 40 eV displacement energy [19,20].

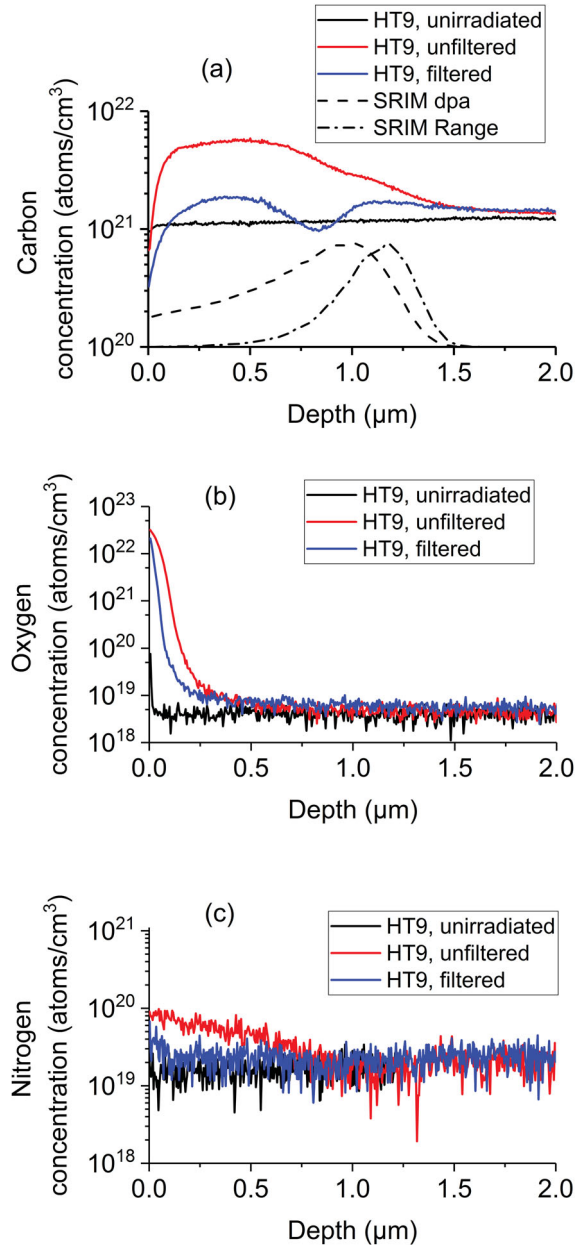


Figure 1. SIMS profiles of (a) carbon, (b) oxygen, and (c) nitrogen in unirradiated and 600 dpa-irradiated HT9, both with and without beam filtering. SRIM-calculated depth profiles of dpa and injected ions are superimposed in Figure 1(a).

Table 1. Composition of HT9(wt%).

Fe	C	Cr	Mo	Si	Mn	Ni	V	W
Bal.	0.21	12.5	1.10	0.29	0.41	0.60	0.30	0.51

Transmission electron microscopy (TEM) specimens were prepared using a TESCAN Lyra focused ion beam mill [18]. Scanning transmission electron microscopy (STEM) high-angle annular dark field (HAADF) and bright field images were obtained using an FEI Tecnai F20 Super Twin operated at 200 kV. TEM lamella thicknesses were measured using a standard electron energy loss spectroscopy technique and were used to calculate void swelling described in an earlier study [18]. Secondary ion mass spectroscopy (SIMS) results were obtained using a Physical Electronics Model 6600 SIMS System with a 4-keV Cs beam for depth profiling of elemental carbon, oxygen, and nitrogen.

Results and discussion

Chemistry modification via Coulomb drag

Figure 1(a) compares SIMS carbon profiles before irradiation and after irradiation to 600 dpa with and without beam filtering. The unirradiated HT9 specimen shows a flat carbon profile with an average concentration of 1.3 at.% C, in good agreement with the specified composition. Without filtering, the carbon concentration after 600 dpa showed enhancement throughout the entire ion range, increasing to a maximum of ~ 7 at.% C at a depth

of 600 nm, followed by a gradual decrease with increasing depth to the nominal concentration in the unirradiated region. The carbon concentration averaged over the irradiated region was ~ 4 at.% C.

The filtered HT9 at 600 dpa exhibited a maximum of ~ 2 at.% C, significantly less than the 7 at.% C in the unfiltered HT9 specimen at the same depth. The carbon profile from the filtered irradiation showed a concentration dip below the background level at 800–850 nm, a depth near the peak damage. The average carbon concentration through the ion-irradiated region is approximately 1.5 at.% C, in close agreement with the unirradiated specimen, indicating that the contamination is greatly minimized by filtering.

The oxygen and nitrogen profiles are provided in Figure 1(b) and (c), respectively. A thin oxide layer was observed after irradiation with a thickness of ~ 20 nm measured by TEM, but the filtered irradiation clearly showed less oxide growth with a thickness of ~ 5 nm. Due to beam knock-on effects during SIMS analysis, however, the tail regions cannot be used to estimate the oxide layer thickness. The nitrogen distribution in the filtered sample shows little difference from the unirradiated sample. In contrast, the unfiltered sample has a significant nitrogen profile with its tail reaching ~ 1 μm depth.

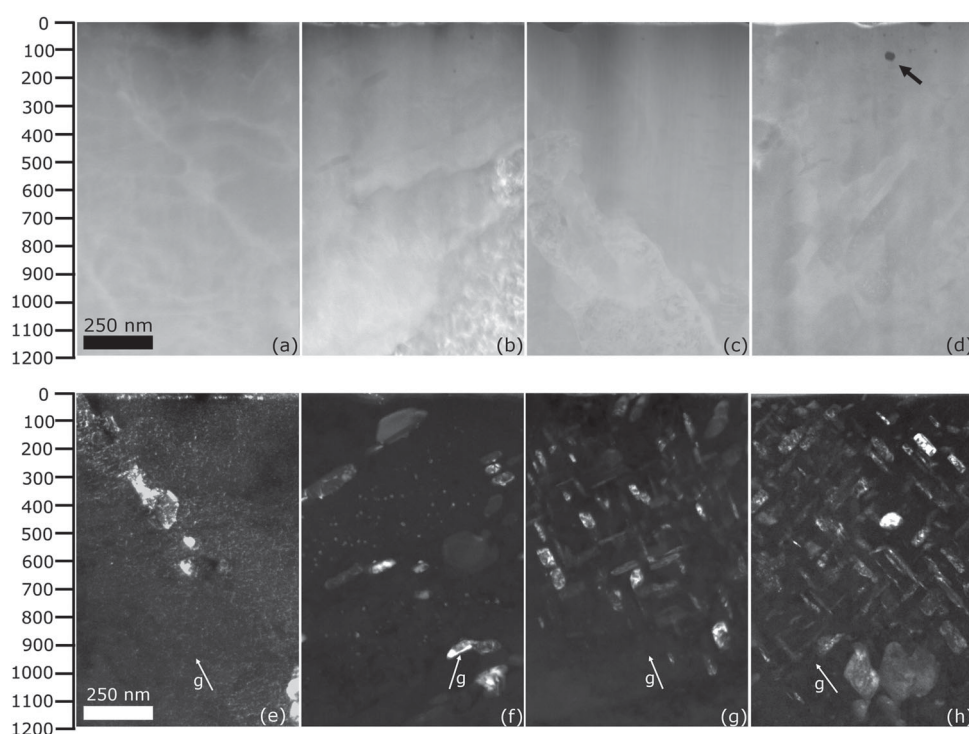


Figure 2. Typical STEM-HAADF (a–d) and dark-field (e–h) images of unirradiated HT9 and HT9 irradiated without filtering to 200, 400, and 600 dpa, respectively. A depth scale to 1200 nm below the surface is provided next to (a,e). The $g = \langle 100 \rangle$ vector is labeled in the dark-field micrographs. A black arrow in (d) marks an isolated large void in the 600 dpa specimen.

Carbon, oxygen, and nitrogen possess different profiles since carbon atoms easily but strongly interact with defects, while oxygen tends to develop strong chemical bonding with surface atoms resulting in a surface oxide layer or oxide particles. Nitrogen, however, does not interact as strongly with defects and diffuses easily. Overall, the filtering system significantly reduced or eliminated carbon, oxygen, and nitrogen contamination.

Void swelling and precipitation

The presence of beam-induced contaminants clearly suppresses void swelling. Figure 2(a) shows the microstructure of unirradiated HT9. Figure 2(b–d) compares STEM images of 200, 400, and 600 dpa samples without filtering. Only a few voids are observed. At doses of 200 and 400 dpa, the void swelling was less than 0.1% and was confined to the first 200 nm below the surface. The

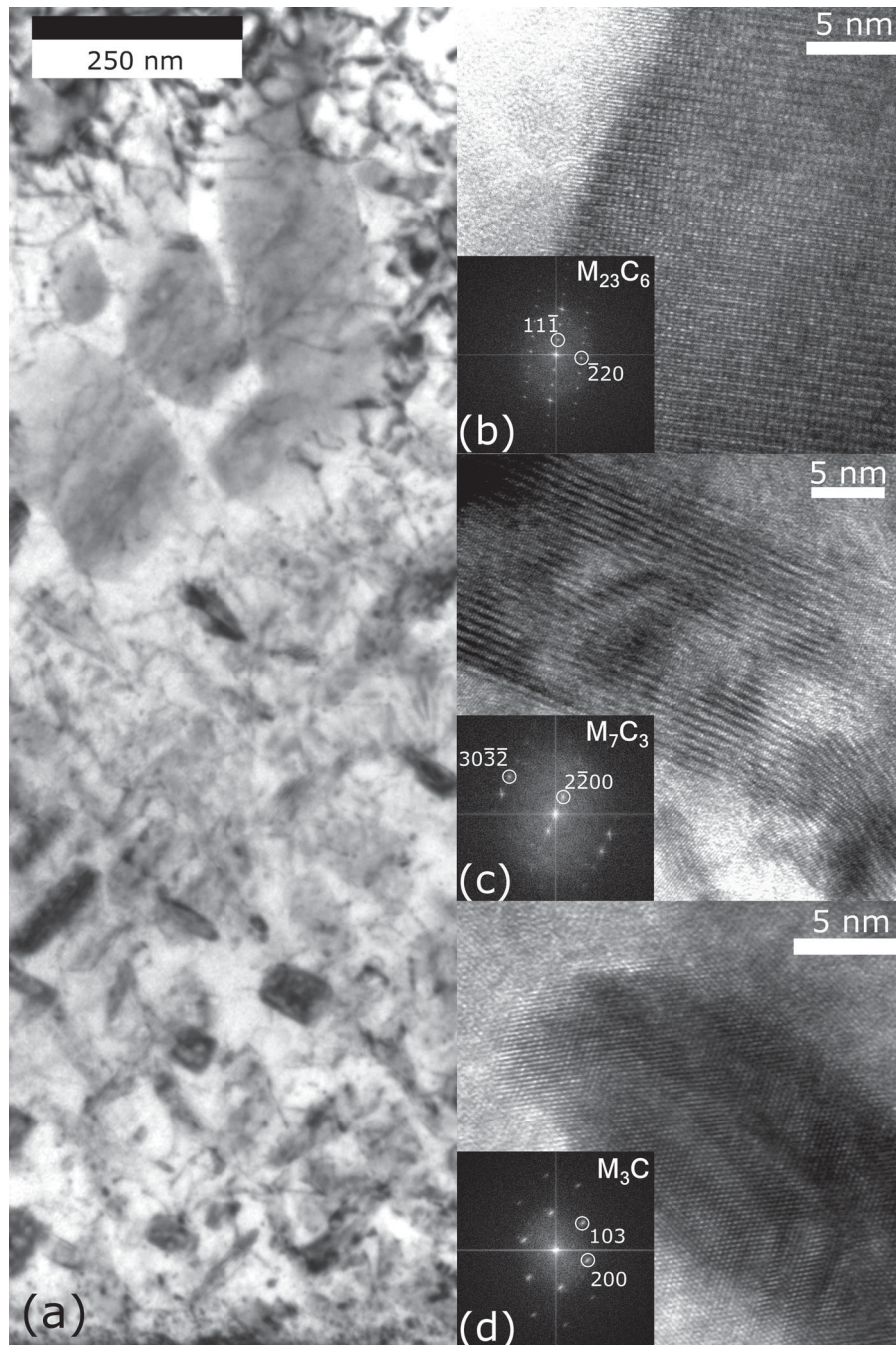


Figure 3. (a) Bright-field TEM image of HT9 irradiated to 600 dpa without filtering, with HRTEM images of (b) $M_{23}C_6$, (c) M_7C_3 , and (d) M_3C particles. Indexed fast Fourier transform images are inset in the respective figures.

appearance of larger voids with $\sim 0.5\%$ swelling occurs at 600 dpa. However, voids were not observed to extend beyond this depth. A previous study has suggested that carbon atoms may alter the effective diffusivity of point defects, leading to dramatic changes in void swelling and void distribution [21]. If vacancy migration energy is slightly increased, void swelling shifts toward the surface. Both the suppressed swelling and shallow void location are believed to be related to carbon content.

Precipitates also play a key role in void swelling and, when present in high densities, can act as recombination sites and greatly suppress swelling [22–24]. Figure 2(e) shows that carbides along grain boundaries are present prior to irradiation, and are present in all irradiated specimens. Figure 2(f–h) shows TEM dark-field images highlighting carbide precipitates that developed in unfiltered HT9 irradiated to 200, 400, and 600 dpa. At 200 dpa, HT9 developed small spherical precipitates ~ 10 – 15 nm in diameter distributed throughout the entire ion range. At 400 dpa, the precipitates increased in size and evolved into needle-like structures with a high aspect ratio (1:3.5) and a diameter of ~ 20 nm and length of 70 nm. The density of carbides was measured to be 0.81×10^{15}

cm^{-3} with a volume fraction of 0.05. A further increase in carbide density to $1.4 \times 10^{15} \text{ cm}^{-3}$ was observed in the 600 dpa specimen where the carbide precipitates were found to comprise a significant volume fraction of 0.12 in the irradiated region.

The majority of the precipitates observed were M_{23}C_6 , M_7C_3 , and M_3C Cr-rich carbides, and are clearly seen in Figures 2(h) and 3(a). Figure 3(b) shows a typical high-resolution TEM (HRTEM) image of an M_{23}C_6 carbide along the [112] zone axis of the particle. These carbides were observed in the unirradiated specimen (Figure 2(e)) along lath boundaries in the tempered martensite phase. After irradiation, M_{23}C_6 carbides appeared within the grains, typically larger than other carbides observed. Plate-like M_7C_3 (Figure 3(c)) and needle-like M_3C carbides (Figure 3(d)) were observed after irradiation and comprised the remainder of precipitates formed as a result of radiation-induced precipitation augmented by the introduction of additional carbon from the beam. HRTEM images of the M_3C precipitate along the [010] zone axis of the particle and M_7C_3 precipitate taken near the $[\bar{5}35]$ zone axis of the matrix are given in Figure 3(d) and (c), respectively. Several irradiations of

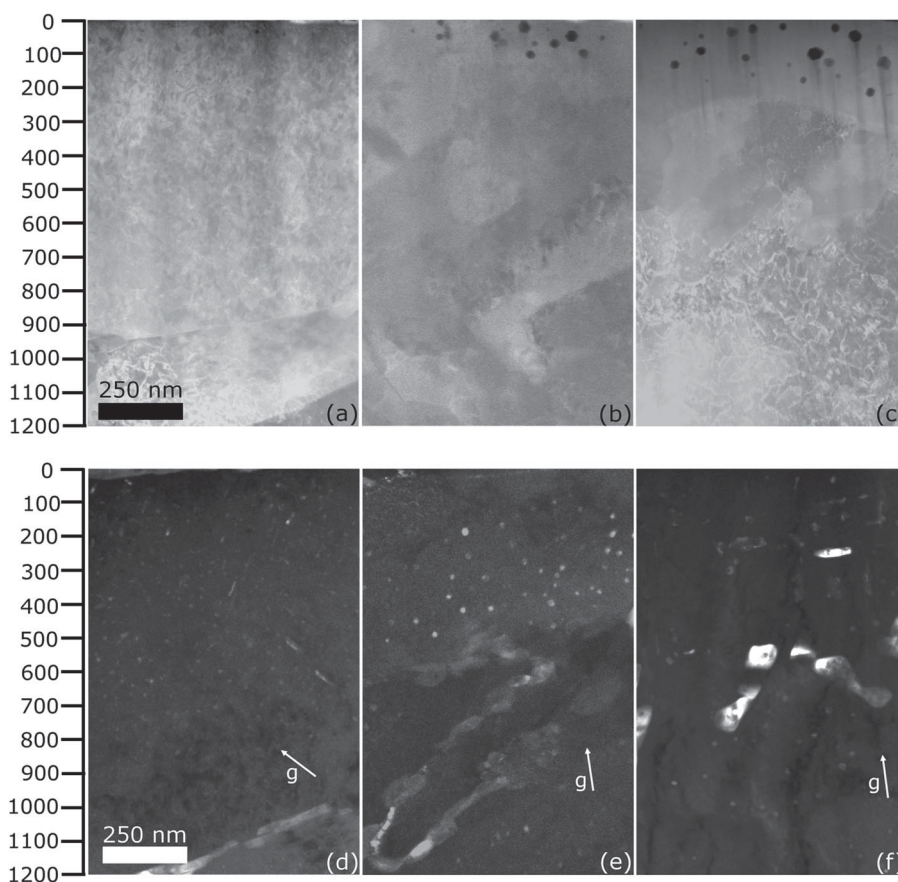


Figure 4. STEM-HAADF (a–c) and dark-field (d–f) images of HT9 irradiated with a filter to 200, 600, and 800 dpa, respectively. The $g = \{100\}$ vector is labeled in the dark-field micrographs.

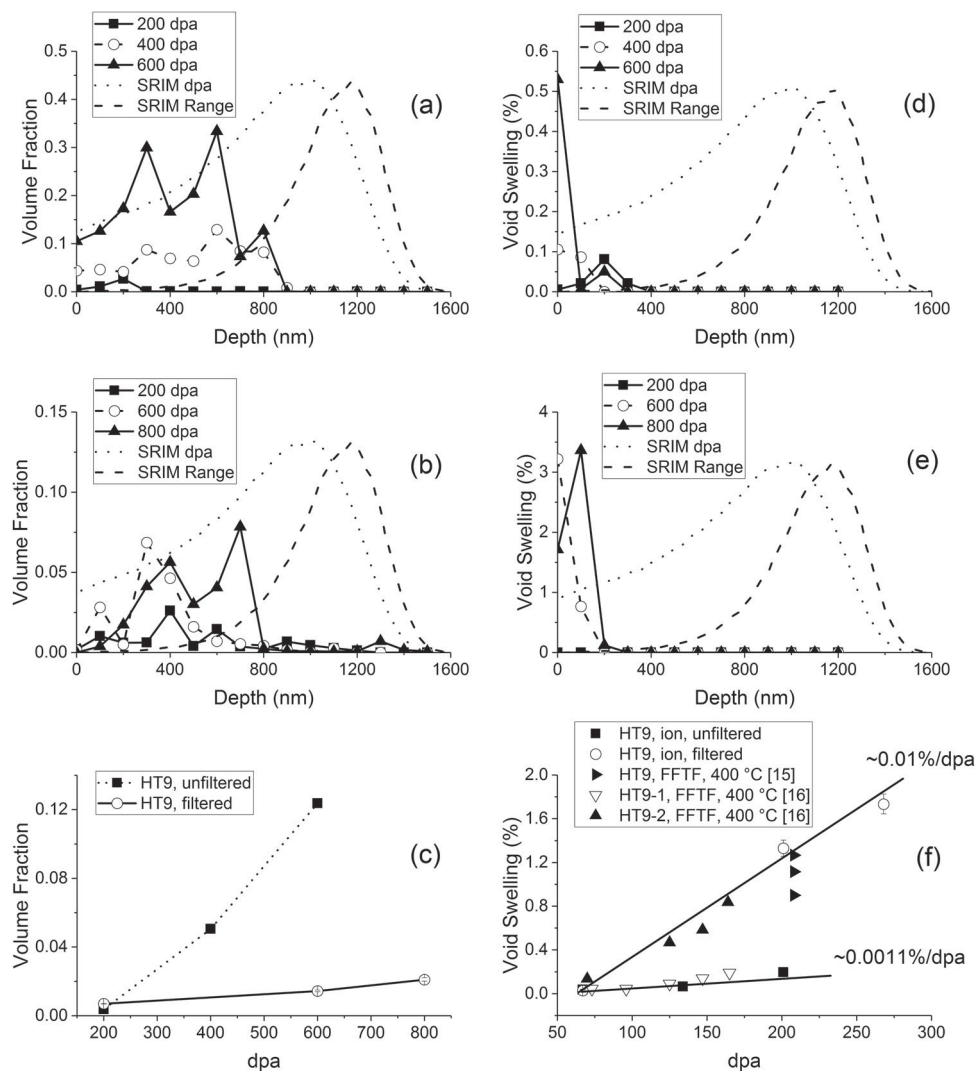


Figure 5. Carbide volume fraction distributions for (a) unfiltered and (b) filtered HT9 irradiations, void swelling distributions for (d) unfiltered and (e) filtered HT9 irradiations, (c) dose-dependent carbide growth rates, and (f) dose-dependent void swelling. Neutron-induced swelling of various HT9 heats provided in (f) [15,16].

HT9 and other F/M alloys at other accelerator facilities have also reported similar precipitation under irradiation and ascribed this to radiation-induced precipitation, contamination, or a combination of both [25,26]. No previous study has attempted to identify and remove the source of the carbon causing the formation of the carbides.

A second irradiation, employing beam filtering, was performed to reach damage levels of 200, 600, and 800 dpa. STEM-HAADF micrographs in Figure 4(a–c) show that the filtering system induced a significant increase in swelling with dramatically different carbide precipitation behaviors in Figure 4(d–f). At 200 dpa, HT9 developed small spherical carbides of similar size and density, along with low swelling observed in the unfiltered counterpart. At 600 dpa, a significant increase in the population of large voids and void density were observed. Furthermore, Figure 4(e) shows a dramatically lower

carbide volume fraction of 0.014, nearly an order magnitude less than the unfiltered irradiated HT9 (Figure 2(h)), without the development of needle-like precipitates. HT9 irradiated to 800 dpa exhibited further increases in void size and density with an inward shift in the swelling and a slight extension of void distribution to deeper depths. Some needle-like carbides were observed to develop within 500 nm of the surface.

The differences in carbide precipitation and growth between unfiltered and filtered specimens are clearly seen in Figure 5(a,b). While both specimens showed carbides throughout the irradiated region, the volume fraction for unfiltered irradiation is greater at all depths compared to the filtered irradiation, differing by a factor of 5 for the maximum volume fraction in the specimens at 600 dpa. The volume fraction growth rate was calculated by averaging the carbide volume fraction plotted against the average dpa in the irradiated region. Figure 5(c)

shows that in the unfiltered specimen, the growth rate is 3.6×10^{-4} volume fraction/dpa, nearly an order of magnitude greater than the rate of 4.7×10^{-5} volume fraction/dpa observed in the filtered specimen.

Figure 5(d,e) provides a comparison of the swelling as a function of depth for unfiltered and filtered irradiations. Void swelling in the filtered HT9 achieved a maximum swelling value ~ 6 times greater than the unfiltered HT9 and reached 100 nm deeper. Since voids were observed to form only within 300 nm of the surface, comparisons of the void swelling in Figure 5(f) are plotted from the average swelling within this region, corresponding to $\sim 35\%$ of the peak dpa. The swelling rate in the filtered HT9 irradiation was calculated to be $\sim 0.01\%/dpa$, approximately an order magnitude greater than the $\sim 0.0011\%/dpa$ measured in the unfiltered HT9. The filtered HT9 void swelling is in good agreement with swelling observed in HT9 after neutron irradiation in most cases [15,16]. That is, HT9 heats with 0.2 wt% carbon exhibited similar swelling behavior to the filtered ion-irradiated HT9. Despite the large variance in neutron-induced swelling, all void swelling and swelling rates are greater than the unfiltered-ion-irradiated HT9, with the swelling rate of the most swelling-resistant HT9 heat (0.17 wt% carbon) approximately twice that of the unfiltered HT9. Furthermore, since F/M alloys are expected to swell at 0.2% per dpa in the steady-state growth stage, the observation of lower swelling rates suggests that swelling is still in the transition stage [3].

This study shows that contamination induced by Coulomb interaction between the beam and residual contaminants plays a dramatic role in void swelling. Without beam filtering, a high density of precipitates was observed within the irradiated region and swelling was greatly suppressed. With beam filtering to avoid/minimize contaminants, precipitate formation was suppressed and void swelling was significantly larger. We assert that swelling suppression arises from carbon and carbides which alter the defect clustering kinetics and act as defect sinks. The present study shows the feasibility of the proposed technique as the best practice to eliminate beam contamination. When evaluating swelling data from previous studies, it will be necessary to assess the possible impact from beam contamination.

Disclosure statement

No potential conflict of interest was reported by the authors.

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