Radiation response of alloy T91 at damage levels up to 1000 peak dpa

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Abstract

Ferritic-martensitic alloys are required for advanced reactor components to survive 500-600 neutron-induced dpa. Ion-induced void swelling of ferritic-martensitic alloy T91 in the quenched and tempered condition has been studied using a defocused, non-rastered 3.5 MeV Fe-ion beam at 475°C to produce damage levels up to 1000 peak displacements per atom (dpa). The high peak damage level of 1000 dpa is required to reach 500-600 dpa level due to injected interstitial suppression of void nucleation in the peak dpa region, requiring data extraction closer to the surface at lower dpa levels. At a relatively low peak damage level of 250 dpa, voids began to develop, appearing first in the near-surface region. With increasing ion fluence, swelling was observed deeper in the specimen, but remained completely suppressed in the back half of the ion range, even at 1000 peak dpa. The local differences in dpa rate in the front half of the ion range induce an "internal temperature shift" that strongly influences the onset of swelling, with shorter transient regimes resulting from lower dpa rates, in agreement not only with observations in neutron irradiation studies but also in various ion irradiations. Swelling was accompanied by radiation-induced precipitation of Cu-rich and Si, Ni, Mn-rich phases were observed by atom probe tomography, indicating concurrent microchemical evolution was in progress. In comparison to other ferritic-martensitic alloys during ion irradiation, T91 exhibits good swelling resistance with a swelling incubation period of about 400 local dpa.

Key words: void swelling, ion irradiation, T91, high dpa, depth dependence, injected interstitial suppression, microchemical evolution

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1. Introduction

For advanced nuclear reactor concepts, there is a critical need for structural materials that can withstand radiation damage levels that are much higher than can be reached by currently used austenitic steels. In the 1970s to 1990s there were a number of national alloy development programs for liquid metal reactors that worked to extend the swelling resistance of austenitic alloys for fast reactor concepts. All programs eventually focused on the use of titanium-modified austenitic steels based on 316 stainless with higher nickel levels, optimized minor element compositions, and improved fabrication procedures for use as fuel cladding and structural components [1,2]. It had been determined earlier, however, that these modified alloys and all austenitic steels would eventually swell at $\sim 1\%/dpa$ at all reactor-relevant temperatures after some incubation dose, with the largest observed incubation delay in the range of 100-150 dpa. It was also observed that alloy optimization would only delay, but not preclude the eventual onset of this higher swelling regime [3-6].

Additionally, it was learned that at $\sim 10\%$ void swelling, austenitic stainless steels developed a new form of severe void-induced embrittlement that became the life-limiting condition for its use as fuel cladding [7-9]. A consequence of this embrittlement was a limitation on fuel burn-up to 10-12%, far short of the $\sim 30\%$ burn-up limitation imposed by fission product accumulation, thereby strongly impacting the economics of power generation in fast reactors. In effect, the economics of power production were dictated by the cladding and not by the much more expensive fuel. To reach optimum higher burn-ups approaching 30% requires materials to be able to withstand 250-350 dpa, depending on the reactor flux-spectra, while some other reactor concepts such as "traveling wave" or actinide "burners" envision doses as high as 400-600 dpa.

It is recognized that one possible solution is to use ferritic or ferritic-martensitic alloys which have been shown to swell much less than austenitic alloys during neutron irradiation [10]. In fact, simple body-centered cubic (bcc) iron-based alloys have longer swelling incubation periods and a lower swelling per dpa rate ($\sim 0.2\%/dpa$) in the steady-state void growth region than do

simple face-centered cubic (fcc) iron-based alloys ($\sim 1.0\%/dpa$) [10,11]. It was also observed that several commercial ferritic-martensitic alloys (HT9 and 9Cr-1Mo) also swelled at $\sim 0.2\%/dpa$ at very high neutron-induced dpa levels of 100-200 dpa.

Odette suggested a number of factors that produce the superior swelling resistance of F/M alloys compared to austenitic alloys [12]. The first proposed mechanism is that the more open bcc lattice results in a lower interstitial bias to dislocations, leading to a lower vacancy population. Additionally, the bcc lattice exists at a higher homologous temperature than the face centered cubic (fcc) lattice, reducing the vacancy supersaturation level that drives void nucleation. Another mechanism postulated by Sniegowski and Wolfer argued the differences in formation and migration energies of vacancies and interstitials in the fcc and bcc iron-base systems might account for the differences in post-transient swelling rate [13]. Most interestingly, before experimental data were available, Sniegowski and Wolfer correctly predicted that bcc iron-base alloys would swell at a lower rate of $\sim 0.2\%/dpa$ compared to the $\sim 1\%/dpa$ characteristic of fcc iron-based alloys.

Other factors have been proposed to account for the lower swelling rate of bcc iron-base alloys. Two prominent types of dislocation loops are observed in bcc iron systems consisting of $a\langle 100 \rangle$ and $a/2\langle 111 \rangle$ loops. Since $a\langle 100 \rangle$ dislocation loops are stronger interstitial sinks compared to $a/2\langle 111 \rangle$ loops, which are neutral sinks for both interstitial and vacancy defects, the bias of interstitials to $a\langle 100 \rangle$ loops results in a larger removal of vacancies by the more dominant $a/2\langle 111 \rangle$ loops [14,15]. The unfaulting of sessile loops and dislocation mobility is also thought to strongly influence swelling behavior. High swelling rates in the transient swelling regime are characterized by the movement of dislocation loops and formation of a complex dislocation network, with steady-state swelling observed afterwards. All of these factors have been proposed as mechanisms that contribute to the swelling resistance under both ion and neutron irradiation.

Second, variations in minor solute concentrations have been observed to influence swelling in bcc iron-base alloys. Experimental studies have shown a strong effect of Cr concentration, with some suggesting that defect trapping by Cr atoms promotes defect recombination and strongly influenced subsequent swelling with the maximum suppression around 12 wt% Cr [16-19].

Minor solute elements, such as Si, Mo, Nb, V, Mn, Ni and C, are also observed to play a role in trapping point defects by producing solute-defect systems that enhance defect recombination [16,20].

In the current study we focus on alloy T91, which is a ferritic/martensitic (F/M) steel that has been used extensively for non-nuclear applications in power plants, typically employed as tubing in boilers, super-heaters, or heat exchangers. There are a handful of investigations using neutron irradiation that reported on the low void swelling behavior of T91 [21-25]. The highest reported dose for this alloy was achieved in the FFTF fast reactor at 208 dpa and yielded a range of void swelling of 2-3% at 400°C for a set of pressurized tubes, with swelling exhibiting some variability within and between individual tubes [25]. For ion-induced swelling tests on T91, the highest reported doses were 140 and 150 dpa, yielding swelling over the range 0.04 to 0.5% in the various experiments [26-28]. In order to explore the suitability of T91 for advanced nuclear applications, it is necessary to explore its swelling behavior to damage levels approaching 500-600 dpa. Since it is impractical to reach any significant fraction of this dose in a reactor, the approach used in this study is to employ self-ion irradiation and compare the results with neutron irradiated T91 and other alloys irradiated with ions under similar conditions. It is important to note, however, that for the extraction of neutron-relevant swelling data at 500-600 dpa, it is necessary to reach peak ion-induced displacement levels of ~1000 dpa due to strong suppression of swelling induced by injected interstitials in the peak dpa region.

2. Experimental Procedure

The heat of alloy T91 used in this study contained 9.4 wt% Cr and minor alloying elements Mo, V, Si, Ni and Nb, with compositional details given in Table 1. The T91 alloy was normalized at 1038°C for 0.5 h, followed by tempering at 760 °C for 0.5 h, with the specimen cooled in air after each step in the heat treatment [27]. The starting microstructure was composed primarily of a tempered martensite phase with grain sizes of ~3-5 μm and an average lath width of ~800 nm. The tempered plate was sectioned into 0.5 mm thick pieces and mechanically ground using 600, 800, and 1200 grit SiC paper. The specimens were then polished further by a 0.05 μm alumina solution followed by electropolishing with a 45% ortho-phosphoric acid, 35% sulfuric acid, and

20% de-ionized water solution for 20 s to remove the surface damage layer produced during mechanical cutting and polishing.

Ion irradiation leads to a non-uniform distribution of damage, increasing in dose rate from the front surface to a peak dpa level and then declining quickly beyond the peak. Irradiation was performed using 3.5 MeV Fe^{2+} ions to achieve peak damage levels of 250, 750, and 1000 dpa, as calculated using the Kinchin-Pease option of the SRIM-2013 code [29]. The calculations used a displacement energy of 40 eV [30]. Note that at 1000 peak dpa, the ion fluence is $\sim 1.1 \times 10^{18}$ ions/cm², adding deposited Fe ions equivalent to ~ 136 nm of additional mass (pure iron) to the back of the ion range, tending to move the ion-incident surface forward by ~ 136 nm. SRIM calculations indicate, however, that sputtering from the front surface will remove ~ 100 nm of material, so that the net change in surface height from these two contributions is relatively small. However, there will be another contribution to elevation of the ion-incident surface arising from the integrated distribution of void swelling.

To avoid the effects of void swelling suppression known to be caused by ion beam rastering [26, 31], a defocused ion beam was utilized [32]. The ion beam was defocused and limited to 200 nA over an area of 6 mm $\times$ 6 mm, yielding a time-averaged peak dpa rate of 1.74×10^{-3} dpa/s and varying less than 5% over the duration of the experiment. F/M steels have previously been irradiated by self-ions at temperatures between 440 °C to 480 °C, a range determined to achieve the maximum swelling for the specimen [26-28,33,34]. In the current study, the specimens were heated to 475°C during ion irradiation by mounting the samples on a copper stage with a hydrocarbon-free silver paste. The beam heating component of the temperature was measured to be $\sim 4\text{-}5^\circ\text{C}$. The specimen temperature was kept to within $\pm 5^\circ\text{C}$ during the irradiation. No pre-implantation or co-implantation of helium and/or hydrogen was employed.

After irradiation, transmission electron microscopy (TEM) specimens were prepared using a focused ion beam (FIB) lift-out technique with a TESCAN LYRA3. Thick lamellae were first prepared by trenching the selected region with a 30 keV Ga^+ beam. Once the lamella was thinned to approximately 1.5 μm , a micro-post was placed near the lamella and attached via Pt deposition. The lamella was then cut from the bulk of the sample, attached to a TEM grid, and

thinned to 300 nm using a lower beam current. Final thinning and polishing of the lamella to a thickness of ~100 nm was performed with a 5 keV Ga⁺ beam. Scanning transmission electron microscopy (STEM), high angle annular dark-field (HAADF), and bright field images of voids were obtained on an FEI Tecnai G20 Super Twin operated at 200 kV. The thicknesses of TEM lamellae were measured using a standard electron energy loss spectroscopy (EELS) technique.

There is a possibility that the depth dependence of swelling may be influenced by segregation-induced compositional changes arising from interaction of solutes with the displacement gradients along the ion range. Therefore, two atom probe tomography (APT) specimens were prepared from the T91 specimen irradiated to 750 peak dpa via a standard lift-out procedure [35] with an FEI Quanta 3D FEG Focus Ion Beam (FIB). The specimen at this dose level was chosen to avoid a heavily voided microstructure while still capturing the impact of an ultra-high damage level. APT specimen fabrication was controlled to a specific region that was within a depth region of 400-600 nm below the ion incident surface, consistent with the depth of greatest interest in this study since the maximum amount of swelling will be shown to occur at this depth at the highest peak damage level of 1000 dpa.

A final cleaning step using 2 kV Ga⁺ beam was carried out to reduce the FIB ion beam damage during specimen fabrication. APT measurements were performed using a local electrode atom probe (LEAP 4000 XHR) at the Environmental and Molecular Sciences Laboratory at Pacific Northwest National Laboratory. All data were collected under vacuum of 1×10^{-11} Torr at 40 K with a detection rate of 0.5 %, laser energy of 70 pJ/pulse, and laser pulse frequency of 200 kHz. The Interactive Visualization and Analysis Software (IVAS) from CAMECA was used for data reconstruction and analysis.

3. Results and discussion

3.1 Void swelling

Fig. 1 (a-c) shows typical STEM-HAADF micrographs after irradiation to 250, 750, and 1000 peak dpa, respectively. Voids were clearly observed in all specimens, but their sizes and distributions varied significantly. At the lowest dose (250 peak dpa), small voids were mainly

located in the near surface region at a depth between 100-300 nm where the local dose ranged from 80 to 100 dpa. At 750 peak dpa, the voids were larger and the void distribution was observed deeper into the specimen at 900-1000 nm where the dose ranged from 725 to 750 dpa. For the highest dose of 1000 peak dpa, larger voids up to ~110 nm in diameter were observed and the void distribution again reached to 900-1000 nm ranging from 950 to 1000 dpa. The average lath width of ~800 nm and grain size of ~3-5 μm observed in the unirradiated T91 was not changed significantly in the T91 specimens irradiated to 250 peak dpa. At 750 and 1000 peak dpa, however, the lath width was observed to increase to ~1 μm , coincident with a large increase in void swelling. A summary of the void statistics averaged over the 400-600 nm range is provided in Table 2.

The expansion of the void distribution from the front near-surface region to a deeper depth with increasing dose has been observed previously [32,36,37] and can be explained by the concept of defect imbalance [36,38]. This phenomenon combines the effects of forward scattering of the incoming ion and that of the injected interstitial effect, both of which are neutron-atypical phenomena arising in self-ion irradiation. Due to forward scattering of interstitials and the extra atoms introduced by ion irradiation, spatial differences arise in the local vacancy and interstitial distributions. The near-surface region is slightly vacancy-rich, while an interstitial-rich region is created near the peak damage region. Thus, void formation is promoted early at shallow depth, while being strongly suppressed in the peak damage region. The highest swelling region eventually lies in-between these two regions, shifting deeper from the surface with increasing damage, but eventually stopping at approximately half of the range of implanted Fe ions. In general, this near-surface swelling behavior has been observed not only in our various studies, but also in those of other researchers [26-28].

Fig. 2 compares the measured void swelling as a function of depth for all three damage levels. Void sizes were measured via TEM, and the void swelling in depth intervals of 100 nm was calculated by using the following equation,

$$V_{\text{swelling}} = \frac{V_{\text{void}}}{V_{\text{region}} - V_{\text{void}}} * 100$$

where V_{void} is the measured void volume, V_{region} is the volume of the 100 nm depth interval, and V_{swelling} is the void swelling. The SRIM-predicted Fe ion range and dpa profiles are also plotted for comparison. Initially, swelling occurred only within 300 nm of the surface, reaching a maximum of ~1% for the 250 peak dpa specimen. At 750 peak dpa, the void swelling reached a maximum of ~6.2% at an approximate depth of 700 nm and 740 local dpa. At 1000 peak dpa, the maximum swelling was ~22% at 550 dpa located between a depth of 450 nm and 550 nm (475 to 625 local dpa), with large voids extending from a depth of 300 nm to 900 nm (420 to 950 local dpa).

Depth-dependent swelling analysis provides additional insight into other possible mechanisms that can influence void swelling. Although the aforementioned defect imbalance effect plays a large role in the observed swelling behavior of ion irradiated materials, there is another neutron-atypical effect that arises from the relatively large variation in the dpa rate over the ion range. Note in Fig. 2 that there is a factor of ~4 increase in dpa rate from the ion-incident surface to the peak damage rate position. Garner and Guthrie [39] suggested that such a difference in dpa rate with depth constituted an "internal temperature shift" that could produce a variation in the duration of the transient regime and/or swelling rate as a function of depth from the surface. It is known that the transient regime of neutron-induced void swelling in austenitic alloys is strongly dependent on dpa rate, increasing in magnitude with increasing dpa rate [1,2]. There is, however, only limited evidence that a similar dependence may occur in neutron-irradiated ferritic iron-base alloys [40]. Earlier studies using several ion-induced damage rates have shown that a similar shift in the transient regime occurs during ion bombardment of austenitic alloys [41-43].

The most dramatic feature of the swelling behavior with depth is the total absence of voids in the region of highest dpa levels. As the dose increases, it can be seen that the injected interstitial effect was gradually overcome, with swelling observed deeper in the foil. However, as the injected population increased more rapidly, voids could not nucleate beyond ~900 nm. Although this absence can be ascribed to the defect imbalance and dpa rate effects mentioned previously, this absence is primarily a consequence of the former on void nucleation, where the incident ion serves as one-half of a Frenkel pair without an accompanying vacancy [44-52]. While this slight

imbalance might seem to be very small, it has been demonstrated theoretically to have a very strong impact on suppression of void nucleation [52].

Fig. 3 provides void swelling values taken from selected depth intervals as a function of the average local damage level in that interval. Swelling was measured from sub-regions of 200-400, 300-500, 400-600, 500-700, and 600-800 nm, each with a 200 nm thickness (compared to 100 nm in Fig. 2) and dose rates of 0.72×10^{-3} , 0.83×10^{-3} , 0.96×10^{-3} , 1.11×10^{-3} , and 1.29×10^{-3} dpa/s, respectively. First, it is clear that swelling at each depth range showed a transient incubation dose with low-rate swelling, followed thereafter by an acceleration in swelling. Second, void swelling, at all dose rates, exhibited an increasing incubation period at deeper depths due to combined effects from both higher local dpa rates and the growing injected interstitial effect. Similar dpa rate or flux effects have been observed previously in ion irradiation [53,54] and neutron irradiation studies [2,25,55,56].

While it is problematic to establish a post-transient swelling rate from only three data points spanning both the transient and post-transient regimes, the highest measured ion-induced swelling rate between the last two high-dose data points is $\sim 0.11\%/dpa$, which is less than the $\sim 0.2\%/dpa$ rate observed for body-centered cubic (bcc) iron-base metals following neutron irradiation. Hence, even at the highest damage level of 1000 peak dpa in this study, the swelling cannot be stated to have fully evolved into the steady-state void swelling stage. However, as shown in Fig. 4, the shift in transient duration with depth in T91 shown in Fig. 3 was also observed by Aydogan *et al.* in a ferritic alloy EK-181 along the ion path as the dpa rate increases [37]. In this case, the post-transient swelling rate was clearly observed to be $\sim 0.2\%/dpa$. Additionally, it should be noted that Aydogan's data in Fig. 4 also show a pronounced extension of the transient regime with increasing depth, arising from the combined influence of increasing dpa rate and increasing influence of the injected interstitial. Our observation of an extension in transient duration with increasing depth and therefore increasing dpa rate was also provided by Whitley and coworkers who irradiated pure nickel with 14 MeV Ni ions [43], providing additional confirmation of the "internal temperature shift" concept.

Other non-rastered ion studies conducted on pure iron [36] and several ferritic-martensitic alloys [33, 57, 58] were observed to develop a post-transient swelling rate of $\sim 0.2\%/dpa$, in agreement with the neutron-induced swelling rate. Two of these observations are shown in Fig 7. These observations of $0.2\%/dpa$ were made on two different accelerators, operating at two different conditions of dpa rate and ion energy, one located in the Ukraine and the other in Texas, signaling the possible reproducibility of this swelling rate in both ion and neutron irradiations.

In a series of recent ion irradiations using rastered beams at the University of Michigan the swelling rates appear to be much lower, proceeding at rates of $\sim 0.03\%/dpa$ or less, possibly reflecting the raster-suppression effect on swelling [26, 59-63]. Indeed, one study in this series involving a direct comparison between raster and no-raster irradiation showed very clearly the strong effect of rastering to suppress swelling at the scanning rates used in that study [26]. A similar study conducted on pure iron at much lower scanning rates also showed raster-suppression of swelling [32]. It is premature at this time, however, to directly ascribe the lower swelling rates only to rastering. Further investigation is required to confirm this possible linkage. As shown in Fig. 2 the highest local swelling for T91 in this experiment is $\sim 22\%$ at 500 nm depth with a local damage level of ~ 550 dpa, suggesting that T91 is a rather swelling-resistant alloy compared to other ferritic or ferritic-martensitic steels. For later comparisons with neutron-irradiated T91 and other ion-irradiated alloys, the depth region from 400-600 nm was chosen to extract swelling data. This depth region exhibited the most swelling, suggesting that it has the least influence from the surface effect and the injected interstitial suppression of void nucleation.

Fig. 5 plots void sizes and void concentration changes as a function of local dpa values. The void statistics are obtained by averaging over the depth region of 400 to 600 nm. Both void sizes and void concentration increase with increasing damage levels, without any indication of saturation. At the highest dose, average void diameters span from ~ 5 nm in the shallow depth region (<400 nm) to an average of ~ 35 nm at deeper depths (400 to 600 nm). While some large voids were observed within this region, on the order of 100 nm, several smaller voids (~ 10 -20 nm) were also present.

Fig. 6 compares the swelling in the region of 400-600 nm with that observed in various neutron irradiation experiments [21-25]. Note that all ion-induced swelling points in Fig. 6 are plotted as a function of local dpa. For 250, 750 and 1000 peak dpa irradiation, the corresponding average dpa values in the void swelling analysis region are 140, 410, and 550 dpa, respectively. The comparison between neutron and ion data in Fig. 6 must recognize that there are variations in composition and fabrication of the various T91 heats for both ion and neutron irradiations. Furthermore, a range of dpa rates from 10^{-8} – 10^{-6} dpa/s were reported for the neutron irradiated specimens depending on the sample position in the reactor core [54,55]. Ignoring differences in composition, however, ion irradiation at high dpa rates (1.7×10^{-3} dpa/s) appears to delay the onset of swelling compared to that under neutron irradiation, again suggesting the likelihood of the dependence of transient duration on dpa rate. As mentioned previously, various studies have shown that increases of dpa rate under both neutron and ion irradiation lead to an extension of the void swelling regime for austenitic alloys [1,2,41,54,55,64,65]. There is one indication that a similar effect occurs in the Russian F/M alloy EP-450 [40], but there is insufficient data at present to ascribe the longer ion-induced transient of T91 (as shown in Fig. 6) solely to the differences in dpa rate.

Fig. 7 compares our results on T91 with various ion irradiated alloys, including one austenitic alloy (18Cr10NiTi) and two F/M alloys (duplex EP-450 and cold-worked HT-9). These three alloys were irradiated at Kharkov Institute of Physics and Technology in the Ukraine by 1.8 MeV Cr^+ ions with a local dose rate of 1×10^{-2} dpa/s at comparable temperatures and also without helium implantation. The 18Cr10NiTi alloy exhibited a steady-state swelling rate of $\sim 1\%$ /dpa after a very short incubation period, in good agreement with neutron data [11,66,67].

Fig. 7 also shows that cold-worked HT-9 exhibited an incubation period of ~ 400 dpa before accelerating to a swelling rate on the order of $\sim 0.2\%$ /dpa, in agreement with behavior expected for F/M alloys [10,33]. This ion-induced swelling rate was also observed in ion-irradiated ferrite grains of duplex alloy EP-450 in the range 150-300 dpa, although the swelling rate of tempered martensite grains was somewhat lower but still increasing at 300 dpa. The swelling rate of T91 appears to be increasing at higher dose, but in this experiment had not yet convincingly approached the anticipated 0.2% /dpa swelling rate, reaching only a maximum of $\sim 0.11\%$ /dpa.

3.1 Microchemical evolution

As addressed earlier, neutron-induced void swelling is sensitive to the overall starting composition and the details of distribution of individual elements. It is also known that radiation causes redistribution of the various elements in both bcc and fcc iron-base alloys and often the redistribution precedes and accompanies the onset of void swelling [1,2]. Additionally, radiation-induced segregation and possible subsequent precipitation caused by ion-induced gradients in dpa levels with depth may modify the local composition vs. depth profiles, as theoretically modeled in several recent papers [69,70]. It should be noted that there is also a significant time-dependent alteration of the composition at the end of range due to the implanted Fe ions, an effect that becomes more pronounced at the high doses explored in this experiment, reaching double-digit concentration levels at 1000 dpa.

Table 3 provides composition data obtained by APT analysis on T91 irradiated to 750 peak dpa taken at depths between 400-600 nm, corresponding to an average local dpa of 410 dpa. For most solutes, there was notable depletion from the matrix compared with the nominal level expected for unirradiated T91, especially for Cr, Mn, and Si. Modelling studies indicate that Cr especially will be redistributed along the ion path [69,70]. Such a large reduction in Cr in the 400-600 nm region is currently thought to be primarily a consequence of the surface and dpa rate gradients, with a lesser influence of precipitation since no significant amount of radiation-altered precipitation was observed. This supposition requires further investigation, however.

On average, both Cu, Mo, and Ni exhibited slight enrichment in this region along with an elevated presence of S. The mechanism for the observed depletion and enrichment of the various solutes is thought to be due to a combination of inverse-Kirkendall and solute-drag effects produced by both the influence of the surface and the dpa rate gradients [69-72]. It can be reasoned from the earlier compositional studies on void swelling that this modification may result in slightly different void swelling behavior than that of the base alloy [17-20]. It is expected, then, that the void swelling at different depths will also respond differently to the evolving depth-dependent differences in composition as the ion irradiation proceeds. In this

paper we present the first results that suggest that microchemical segregation arising from both dpa gradients and precipitation may play a role in the observed swelling vs. depth profiles.

From Fig. 8, it can be readily seen that there are a few precipitates enriched in Si, Ni, Mn, and Cu within the analysis volume. Differences in solute concentrations suggested that there are two kinds of precipitates. The precipitates labeled A are primarily composed of Ni, Si, and Mn with a slight enrichment of S. It is possible that some of these precipitates may have formed during metallurgical production from the addition of Mn to remove S from the matrix during fabrication. However, these precipitates have also been observed to form in T91 at low proton and self-ion doses [73], suggesting these to be primarily the result of irradiation. Precipitates labeled B are rich in Si, Ni, Mn, and Cu, enrichments similar to an intermetallic phase known as the G-phase that can form in both irradiated ferritic and austenitic alloys.

Fig. 9 provides solute mapping similar to Fig. 7 on a second APT tip, but extends the analysis to both Cr and P. There are two readily observed precipitate sizes seen in the reconstructed data. The smaller precipitates were found to be similar in composition to those precipitates labeled A in Fig.8. The larger precipitate was Cu-rich with an enrichment of Si, Ni, Mn, and Cr. This precipitate featured a complex structure and showed Cu enrichment near its periphery with a Si and P-rich core. Precipitates of this size and structure were notably absent in the first tip.

Both Figs. 8 and 9 clearly show radiation-induced precipitation occurring in T91 at a high damage level. While precipitation was observed in neutron-irradiated T91 [23], the gradients of dpa rate in ion irradiations, the injection of ions, and the physical discontinuity at the surface may introduce three new modes of segregation that probably affect precipitation behavior. Ultimately, these segregation processes may synergistically influence swelling through interaction with other neutron-atypical processes, especially the strong influence of dpa rate differences and defect imbalance effects.

Conclusions

We used 3.5 MeV Fe self-ion irradiation to investigate the swelling response of T91 under radiation damage levels up to 1000 peak dpa. Maximum swelling occurred at approximately half

of the projected ion range due to the defect imbalance effect. Due to the very strong influence of injected interstitial suppression of void nucleation, even 1000 dpa is insufficient to allow voids to form in the peak dose region. Swelling of T91 had an ion-induced incubation period of swelling of ~400 dpa at the depth of peak swelling, significantly greater than that observed for neutron irradiations conducted at much lower dpa rates. A maximum swelling of ~22% was measured at the local damage level of 550 dpa. Furthermore, it was observed that radiation-induced segregation and precipitation of Cu-rich and Si, Ni, Mn-rich phases occurred in the depth region investigated corresponding to 410 average local dpa, and is similar to phases observed in ferritic steels after ion or neutron irradiation. These findings highlight T91's relatively high swelling resistance compared with various other ferritic-martensitic alloys, especially including HT-9 and EP-450.

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Captions

Figure 1 - Typical STEM-HAADF micrographs of selected areas of T91 ion irradiated to a peak dose of (a) 250, (b) 750, and (c) 1000 dpa. An overlay of the SRIM-calculated ion range and damage distribution curves is provided in (a).

Figure 2 - (a) Profiles of dpa and Fe implanted ion distributions from SRIM calculations plotted for a dose of 1000 peak dpa. Arrows next to curves indicate the respective axes. (b) Void swelling as a function of depth for T91 specimens irradiated to peak dose of 250, 750, and 1000 dpa. Local swelling levels were calculated for 100 nm intervals of depth.

Figure 3 - Void swelling as a function of local damage level averaged over selected depth intervals of 200 nm thickness with swelling rates of 0.1 and 0.2%/dpa included on the figure for comparison. The transient period of swelling appears to increase with increasing dpa rate.

Figure 4 - Swelling of (a) annealed and (b) severely deformed EK-181 as a function of dpa but extracted from different depth regions. These irradiations were performed under conditions identical to that used for T91 in the current study. The tendency to approach a swelling rate of ~0.2%/dpa and also to exhibit longer transient duration before changing to the 0.2%/dpa rate with increasing depth are clearly shown. Data were provided by E. Aydogan in advance of publication [37].

Figure 5 - Plot of the average void radius and concentration as a function of local dpa for the depth region of 400 nm to 600 nm. Arrows are shown to indicate corresponding axis.

Figure 6 - A comparison between the swelling behavior of T91 irradiated in FFTF [21-25] and that of ion-irradiated T91 at a depth of 400-600 nm (present study).

Figure 7 - Comparison of the void swelling in T91 with that of other ion-irradiated alloys.

Figure 8 - Solute distribution obtained by APT from the first tip prepared from the T91 specimen irradiated to 750 peak dpa, showing two types of precipitates. Note that the red border at the top indicates the ion- incident surface. The tip length shown above is approximately 95 nm.

Figure 9 - Solute distribution obtained by APT from the second tip prepared from the T91 specimen irradiated to 750 peak dpa, showing two types of precipitates. Note that the red border indicates the ion-incident surface. The tip length is approximately 40 nm.

Table 1 - Composition of T91 used in this study.

	Fe	Cr	Mo	V	Mn	C	Si	Cu	Ni	Al	Nb	N	P	S
wt%	Balance	9.38	0.91	0.19	0.38	0.085	0.34	0.08	0.097	0.032	0.08	0.042	0.019	0.0008

Table 2 - Void characteristics from the current study. Maximum void swelling and local swelling at the interval of 500 nm $\pm$ 100 nm below the surface are provided for each set of samples. The dpa level, void radius and void concentration are averaged within the interval.

Peak dpa	Maximum void swelling (%)	Void swelling at 400-600 nm (%)	Average void radius (nm)	Average void concentration ($10^{14}/\text{cm}^3$)
250	1.00 ± 0.06	0.04 ± 0.01	12.0 ± 4.79	0.68 ± 0.04
750	6.20 ± 2.15	2.77 ± 0.96	17.3 ± 6.97	2.55 ± 0.27
1000	22.5 ± 2.22	17.3 ± 1.86	37.8 ± 6.99	4.58 ± 0.05

Table 3 - Composition of T91 obtained by APT at a depth from 400-600 nm. The measured composition for unirradiated T91 for selected solutes is provided for comparison.

wt%	Cr	Mo	Mn	V	Nb	Ni	Si	Cu	C	S
Tip #1	2.62	1.41	0.05	0.23	0.00	0.10	0.01	0.05	0.00	0.005
Tip #2	2.80	0.68	0.10	0.16	0.00	0.34	0.01	0.11	0.00	0.01
Nominal	9.38	0.91	0.38	0.19	0.08	0.097	0.34	0.08	0.085	0.0008

Figure 1 - Typical STEM-HAADF micrographs of selected areas of T91 ion-irradiated to a peak dose of (a) 250, (b) 750, and (c) 1000 dpa. An overlay of the SRIM-calculated ion range and damage distribution curves is provided in (a).

Figure 2 – (a) Profiles of dpa and Fe implanted ion distributions from SRIM calculations plotted for a dose of 1000 peak dpa. Arrows next to curves indicate the respective axes. (b) Void

swelling as a function of depth for T91 specimens irradiated to peak dose of 250, 750, and 1000 dpa. Local swelling levels were calculated for 100 nm intervals of depth.

Figure 3 - Void swelling as a function of local damage level averaged over selected depth intervals of 200 nm thickness with swelling rates of 0.1 and 0.2%/dpa included on the figure for comparison. The transient period of swelling appears to increase with increasing dpa rate.

Figure - 4 Swelling of (a) annealed and (b) severely deformed EK-181 as a function of dpa but extracted from different depth regions. These irradiations were performed under conditions identical to that used for T91 in the current study. The tendency to approach a swelling rate of

~0.2%/dpa and also to exhibit longer transient duration before changing to the 0.2%/dpa rate with increasing depth are clearly shown. Data were provided by E. Aydogan in advance of publication [37].

Figure 5 - Plot of the average void radius and concentration as a function of local dpa for the depth region of 400 nm to 600 nm. Arrows are shown to indicate corresponding axis.

Figure 6 – A comparison between the swelling behavior of various heats of T91 irradiated in FFTF [21-25] and that of ion-irradiated T91 at a depth of 400-600 nm (present study).

Figure 7 - Comparison of the void swelling in T91 with that of other ion-irradiated alloys.

Figure 8 – Solute distribution obtained by APT from the first tip prepared from the T91 specimen irradiated to 750 peak dpa, showing two types of precipitates. Note that the red border at the top indicates the ion-incident surface. The tip length shown above is approximately 95 nm.

Figure 9 - Solute distribution obtained by APT from the second tip prepared from the T91 specimen irradiated to 750 peak dpa, showing two types of precipitates. Note that the red border indicates the ion-incident surface. The tip length is approximately 40 nm.

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