The Role of Hydrogen in the Synergistic Effect Between Hydrogen and Displacement Damage on Defect Formation in RAFM Steel

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Abstract

The presence of hydrogen affects the formation of irradiation defects in reactor structural materials, which in turn influences the degradation of their mechanical properties. A deeper understanding of the mechanisms underlying irradiation effects in structural materials in the presence of hydrogen represents an important scientific challenge in the field of fusion and fission energy. Reduced-activation ferritic/martensitic (RAFM) steel, a potential structural material for fusion and fission reactors, was selected as the research material. Using positron annihilation Doppler broadening spectroscopy, it was characterized that a significant number of hydrogen atoms in hydrogen-irradiated RAFM steel are trapped at vacancies, resulting in the formation of relatively stable vacancy-H complexes. Furthermore, first-principles calculations revealed that this hydrogen trapping behavior at vacancies inhibits the recombination of vacancies and self-interstitial atoms (SIAs) generated by cascade collisions, especially when the hydrogen concentration is high, thereby promoting the formation of irradiation defects.

Full Text

Preamble

The Role of Hydrogen in the Synergistic Effect Between Hydrogen and Displacement Damage on Defect Formation in RAFM Steel

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Abstract

The presence of hydrogen affects the formation of irradiation defects in reactor structural materials, which in turn influences the degradation of their mechanical properties. Developing a deeper understanding of the mechanisms behind irradiation effects in structural materials containing hydrogen represents an important scientific challenge for both fusion and fission energy systems. Reduced-activation ferritic/martensitic (RAFM) steel, a potential structural material for fusion and fission reactors, was selected as the research material for this study. Using positron annihilation Doppler broadening spectroscopy, we characterized that a significant number of hydrogen atoms in H^+-irradiated RAFM steel are captured in vacancies, resulting in the formation of relatively stable vacancy-H complexes. Furthermore, first-principles calculations revealed that this capture of hydrogen atoms at vacancies inhibits the recombination of vacancies and self-interstitial atoms (SIAs) generated by cascade collisions, especially at high hydrogen concentrations, thereby promoting the formation of irradiation defects.

Keywords: Vacancy-H complexes; Irradiation defect; Synergistic effect; Positron annihilation DBS; RAFM steel

1. Introduction

Reduced-activation ferritic/martensitic (RAFM) steel is considered a leading candidate for structural materials in fusion and fission energy systems, owing to its superior mechanical properties and enhanced resistance to irradiation [1-3]. In reactors, bombardment by high-energy neutrons generated from nuclear reactions leads to the accumulation of displacement damage, resulting in a series of irradiation effects such as swelling, hardening, and embrittlement [3].

Furthermore, neutron bombardment is accompanied by (n, p) nuclear transmutation reactions that generate hydrogen. Additional hydrogen production occurs through environmental sources, including corrosion, radiolytic decomposition, and recoil injection, particularly in systems involving water cooling and moderation [4]. The presence of significant amounts of hydrogen exacerbates

irradiation effects caused by the accumulation of displacement damage, necessitating consideration of synergistic effect mechanisms rather than focusing solely on displacement damage alone. Therefore, gaining a deeper understanding of irradiation mechanisms in structural materials containing hydrogen poses an important scientific challenge for current fusion and fission energy systems [5-6].

Given the high diffusivity of hydrogen in metals, it was initially believed that hydrogen would not influence the generation of irradiation effects. However, as more studies involving multiple ion irradiations emerged, experimental results indicated that hydrogen presence has a notable influence on irradiation effects. This influence primarily manifests in the fact that hydrogen introduction during displacement damage generation significantly promotes the nucleation and growth of voids, thereby greatly increasing material swelling rates [5-12]. For example, in experiments reported by Clowers et al., the swelling rate of an Fe8Cr2W model alloy with hydrogen present was 3.6 times greater than without hydrogen [6]. However, the exact mechanism by which hydrogen promotes defect formation has not been thoroughly studied. One challenge is that existing experimental techniques have difficulty detecting and tracking hydrogen, making it hard to ascertain its role in irradiation defect formation. Even the most widely used defect study method, transmission electron microscopy (TEM), can only observe voids, and characterizing hydrogen presence within these voids is particularly difficult.

Positron annihilation spectroscopy has been widely used to characterize irradiation defects and is particularly effective at identifying vacancy defects [13]. Although this method faces challenges in directly characterizing hydrogen within materials, it is highly sensitive to hydrogen occupation in vacancies. In this study, positron annihilation Doppler broadening spectroscopy (DBS) was employed to characterize defects in RAFM steel after H^+ and Ar^+ irradiation, aiming to investigate hydrogen's influence on irradiation defect formation. Additionally, the defect evolution behavior of irradiated RAFM steel was characterized through positron annihilation DBS after annealing at different temperatures, combined with first-principles calculations to explore the mechanisms by which hydrogen affects defect formation.

2.1. Sample Preparation and Ion Irradiation

The RAFM steel utilized in this study was supplied by the Institute of Nuclear Energy Safety Technology [14]. The steel compositions are shown in Table 1. The heat treatment process consisted of normalizing at 1000 °C for 40 minutes, followed by water cooling, then tempering at 740 °C for 90 minutes with subsequent air cooling. The bulk RAFM steel was cut into 10$×10×$1 mm sheets, and their surfaces were mechanically polished. The surfaces were then electropolished using a mixture of 5% perchloric acid and 95% ethanol at a temperature of 243 K.

The prepared eight sheet samples were divided into two groups of four samples

each. One group was irradiated with 6.7 keV H^+ to a fluence of 5×10^{20} H^+ m^{-2}, while the other group was irradiated with 160 keV Ar^+ to a fluence of 8.5×10^{18} Ar^+ m^{-2}. The irradiation was performed at room temperature. The irradiation energies of H^+ and Ar^+ were selected to ensure that the peak damage dose from both ion irradiations occurred at the same depth in the samples. From each group, three samples were annealed for 30 minutes at temperatures of 373 K, 473 K, and 573 K, respectively. Annealing was conducted in a vacuum chamber with a pressure of $\leq 2 \times 10^{-4}$ Pa. Sample temperature during annealing was monitored using a thermocouple, with temperature fluctuations of $±$3 K.

[Figure 1: see original paper]

The damage dose and atom concentration distribution produced by ion irradiation in the samples were simulated using SRIM-2008 software, with results shown in Figure 1. The model used for SRIM-2008 calculations was the "Ion Distribution and Damage Quick Calculation" model [15]. For 6.7 keV H^+ irradiation at a fluence of 5×10^{20} H^+ m^{-2}, the damage dose peak (DP) is located at a depth of 33 nm with a value of ~0.2 dpa, and the atom concentration peak (CP) is located at a depth of 57 nm with a value of 93,000 appm. For 160 keV Ar^+ irradiation at a fluence of 8.5×10^{18} Ar^+ m^{-2}, the DP is located at a depth of 34 nm with a value of ~1.0 dpa, and the CP is located at a depth of 76 nm with a value of 1,320 appm.

2.2. Positron Annihilation DBS

Microstructural changes in the irradiated and annealed samples were analyzed using positron annihilation DBS with a slow positron beam at the Institute of High Energy Physics. The positron source was 1.85 GBq ^{22}Na, and the positron beam energy range spanned from 0 to 20 keV. The depth of incident positrons was determined using the equation from reference [16], where Z represents the incident depth (nm), E represents the incident energy (keV), and $= 7.805 \times 10^3$ kg/m^3 is the density of Fe-9Cr from the SRIM calculation results.

In DBS, the Doppler broadening of positron annihilation radiation at the 511 keV peak was measured using a high-purity germanium detector. The S and W parameters were used to evaluate DBS changes. The S parameter indicates the proportion of the central low-momentum region (510.2–511.8 keV) to the full peak (504.2–517.8 keV), while the W parameter represents the proportion of the high-momentum wings (504.2–508.4 keV and 513.6–517.8 keV) to the total peak.

2.3. First-Principles Calculations

A bcc supercell containing 128 iron atoms ($4 \times 4 \times 4$ unit cells) was used for first-principles calculations based on density functional theory (DFT) in the Vienna Ab initio Simulation Package (VASP) [17-18]. DFT calculations were performed using plane-wave basis sets and projector-augmented wave (PAW)

potentials [17, 19]. Exchange-correlation interactions were treated using the generalized gradient approximation (GGA) in the Perdew-Burke-Ernzerhof (PBE) formulation for all calculations [17, 20]. Valence electrons considered were Fe ($3d^7$ $4s^1$) and H ($1s^1$). A plane-wave cutoff energy of 400 eV was applied with a Monkhorst-Pack grid of $3 \times 3 \times 3$. Forces on all atoms were minimized to below 0.01 eV/Å, and energy optimization continued until variation converged to 10^{-5} eV.

3.1. Positron Annihilation DBS

[Figure 2: see original paper]

Positron annihilation DBS results for unirradiated, H^+-irradiated, and Ar^+-irradiated samples are presented in Figure 2. Figure 2(a) shows the S parameter versus positron incident energy (S-E curves). For the unirradiated sample, the S parameter decreases significantly with increasing positron incident energy and eventually levels off, which is characteristic of annealed metallic samples [21]. The S-E curve for the H^+-irradiated sample exhibits a unimodal shape, peaking at a positron incident energy of 2.18 keV (depth of 18 nm). In contrast, the S-E curve for the Ar^+-irradiated sample exhibits a bimodal shape with peaks at incident energies of 2.68 keV (depth of 25 nm) and 5.68 keV (depth of 90 nm). The peak of the S-E curve for the H^+-irradiated sample is located close to the first peak of the S-E curve for the Ar^+-irradiated sample.

Figure 2(b) displays the W parameter versus positron incident energy (W-E curves). For each sample, the W parameter typically exhibits a trend opposite to that of the S parameter. The W parameters for unirradiated, H^+-irradiated, and Ar^+-irradiated samples gradually increase with rising positron incident energy. Compared to the unirradiated sample, W parameters for H^+- and Ar^+-irradiated samples show significant decreases. For the H^+-irradiated sample, W parameters are lower than those of the Ar^+-irradiated sample at depths less than 47 nm, but higher at depths greater than 47 nm.

Figure 2(c) shows S-W plots for unirradiated, H^+-irradiated, and Ar^+-irradiated samples, with each sample having 29 (S, W) points. The (S, W) points for the unirradiated sample distribute linearly with a fitted slope of -0.79. For the other samples, (S, W) points were fitted linearly for segments from the first to second point, second to fifth point, and fifth to twenty-ninth point, yielding three segments L1, L2, and L3 for each sample. The slopes of the three segments for the H^+-irradiated sample are approximately -0.24, 0.46, and -0.65, respectively. For the Ar^+-irradiated sample, the slopes are approximately -1.28, 0.18, and -0.62. All fitted segment slopes are summarized in Table 2. The three line segments obtained from fitting the (S, W) points of the H^+-irradiated sample exhibit an “L” shape, while those of the Ar^+-irradiated sample exhibit a “Z” shape.

[Figure 3: see original paper]

Figures 3(a) and (b) show S parameters versus positron incident energy for H^+- and Ar^+-irradiated samples after annealing at 373 K, 473 K, and 573 K, respectively. The S parameters of annealed samples remain larger than those of unirradiated samples in the irradiation region, except in the near-surface region of 0–10 nm. As shown in Figure 3(a), compared to the as-irradiated H^+ sample, there is no significant variation in S parameters after annealing at 373 K. However, after annealing at 473 K, S parameters show a notable increase near the DP region, while after annealing at 573 K, S parameters show a significant decrease in the irradiation region. In Figure 3(b), compared to the as-irradiated Ar^+ sample, S parameters exhibit no significant changes near the DP region after annealing at 373 K, but show a marked decrease near the CP region. After annealing at 573 K, the S parameter shows a significant decrease throughout the irradiation region.

[Figure 4: see original paper]

Figures 4(a) and (b) show W parameters versus positron incident energy for H^+- and Ar^+-irradiated samples after annealing at different temperatures. After annealing, W parameters remain lower than those of unirradiated samples in the irradiation region, except in the near-surface region (0–10 nm). As shown in Figure 4(a), compared to the as-irradiated H^+ sample, W parameters show no significant changes after annealing at 373 K and 473 K, but increase significantly in the irradiation region after annealing at 573 K. In Figure 4(b), relative to the as-irradiated Ar^+ sample, W parameters show little difference in the near-surface region after annealing at 373 K, but exhibit a significant increase in the deeper region. After annealing at 473 K, W parameters show no significant changes near the DP region but a notable increase near the CP region. After annealing at 573 K, W parameters show a significant increase throughout the irradiation region.

[Figure 5: see original paper]

Figures 5(a) and (b) show S-W plots for H^+- and Ar^+-irradiated samples after annealing at 373 K, 473 K, and 573 K. For each annealed sample, the 29 (S, W) points were used to perform linear fits from the first to second point, second to fifth point, and fifth to twenty-ninth point, yielding three line segments L1, L2, and L3.

For H^+-irradiated samples, the slopes of the three segments after annealing at 373 K are approximately -0.36, 0.30, and -0.63. After annealing at 473 K, the slopes are approximately -0.99, 0.65, and -0.59. After annealing at 573 K, the slopes are approximately -0.45, 0.19, and -0.61. For Ar^+-irradiated samples, the slopes after annealing at 373 K are approximately -1.08, 0.08, and -0.65. After annealing at 473 K, the slopes are approximately -1.06, 0.05, and -0.62. After annealing at 573 K, the slopes are approximately -0.97, 0.66, and -0.76. The (S, W) points for H^+-irradiated samples after annealing at 373 K and 473 K both exhibit “L” shapes, while those after annealing at 573 K exhibit a “Z” shape. In contrast, the (S, W) points for Ar^+-irradiated samples after annealing at 373

K, 473 K, and 573 K all exhibit “Z” shapes.

3.2. First-Principles Calculations

[Figure 6: see original paper]

To gain fundamental understanding and atomistic insight into hydrogen’s impact on defect formation in the synergistic effects of displacement damage, first-principles calculations were conducted. A body-centered cubic (bcc) supercell containing 128 iron atoms (4 × 4 × 4 unit cells) was constructed by moving an iron atom from the body-centered position to a neighboring interstitial site, creating a vacancy and a self-interstitial atom (SIA) defect, as shown in Figure 6(a1). After relaxing this model, the vacancy and SIA recombined, as illustrated in Figure 6(b2).

When 1 to 5 hydrogen atoms were added to the vacancy in the model shown in Figure 6(a1), relaxation results indicated that the SIA combined with the vacancy for 1 to 4 hydrogen atoms, as shown in Figures 6(a2-a5) and (b2-b5). However, when the number of hydrogen atoms in the vacancy increased to 5, relaxation results showed that vacancy-SIA combination was inhibited, forming a crowdion SIA and a Vac-H_5 complex, as depicted in Figures 6(a6) and (b6). Furthermore, when the number of hydrogen atoms was increased to 6 or 7, vacancy-SIA combination was similarly inhibited.

4.1. As-Irradiated RAFM Steel

Compared to the unirradiated sample, S parameters of H^+- and Ar^+-irradiated samples increased while W parameters decreased, as shown in Figures 2(a) and (b). This occurs because H^+ irradiation introduces three types of defects: vacancies, SIAs, and hydrogen atoms, while Ar^+ irradiation introduces vacancies, SIAs, and argon atoms. The presence of high concentrations of vacancies and SIAs causes S parameters to increase and W parameters to decrease, respectively [13, 22]. Interestingly, the S-E curve for the H^+-irradiated sample displays a unimodal shape, while that for the Ar^+-irradiated sample shows a bimodal shape.

SRIM calculations indicate that ion irradiation creates a DP and a CP in the samples, with the former located closer to the sample surface. The peak of the S-E curve for the H^+-irradiated sample is situated near the DP region. In contrast, the first peak of the S-E curve for the Ar^+-irradiated sample is near the DP region, while the second peak is near the argon CP region. This suggests that after H^+ irradiation, vacancy defects are enriched primarily in the DP region, whereas after Ar^+ irradiation, vacancy defect enrichment occurs near both the DP and the argon CP.

The enrichment of vacancy defects after H^+ irradiation is due to vacancies generated by cascade collisions. Additionally, the S-E curve for the H^+-irradiated sample does not show a peak near the hydrogen concentration peak despite the

high hydrogen concentration, indicating no hydrogen enrichment in that region. This is likely related to hydrogen's high diffusivity in metals.

The first vacancy defect enrichment region in the Ar^+-irradiated sample arises from vacancies generated by cascade collisions. Research by Gai et al. indicates that adding extra Ar atoms to Vac-Ar clusters causes Fe atoms in neighboring lattice sites to be ejected as SIAs, thereby increasing the number of vacancies in Vac-Ar clusters [23]. Based on these findings, the second vacancy defect enrichment region may be attributed to accumulation of a high concentration of Ar atoms near the CP, which triggers the SIA ejection mechanism, producing both vacancy and SIA defects. However, the stability of these defects is relatively low. As shown in Figure 3(b), S parameters decrease significantly in the Ar CP region during annealing at 373 K, indicating these vacancy and SIA defects can easily recombine. Thus, due to most Ar atoms accumulating in the CP region following Ar^+ irradiation, their involvement in vacancy and SIA defect formation near the DP region is minimal.

It is noteworthy that the displacement damage peak values produced by H^+ and Ar^+ irradiation are 0.2 dpa and 1 dpa, respectively, with the latter being five times greater than the former. However, DBS results indicate that the S-E curve for the H^+-irradiated sample is slightly higher than that for the Ar^+-irradiated sample in the DP region, while the W-E curve for the former is significantly lower than that for the latter, as shown in Figures 2(a) and (b). For the same material, a larger S parameter indicates a higher quantity of vacancy-type defects, while a smaller W parameter indicates a higher quantity of interstitial-type defects. This suggests that although H^+ irradiation produces less displacement damage than Ar^+ irradiation, it generates more vacancy and SIA defects in the DP region.

The displacement damage value represents the average number of displacements per atom. Each displaced lattice atom creates a Frenkel defect consisting of one vacancy and one SIA. However, a significant number of vacancies and SIAs generated during cascade collisions in the ion irradiation process will recombine, with the recombination rate considered to be ~70% or higher [24-26]. In other words, compared to Ar^+ irradiation, more vacancies and SIAs produced by cascade collisions survive under the same displacement damage dose in H^+ irradiation.

Since vacancy and SIA defect formation near the DP region in Ar^+-irradiated samples is primarily driven by cascade collisions, the greater number of these defects in the DP region of H^+-irradiated samples should be attributed to hydrogen's influence on their formation during cascade collisions. Hydrogen presence indeed plays a significant role in defect formation. In experimental reports by Clowers et al., the irradiation swelling rate of an Fe8Cr2W model alloy with hydrogen participation was 3.6 times higher than without hydrogen [6]. Furthermore, Jiang et al.'s studies on dual ion beam irradiation of Cr with Fe^+ and H^+ demonstrated that H^+ co-injection with Fe^+ led to significant void growth [12].

4.2. Annealing of Irradiated RAFM Steel

S parameters of Ar^+-irradiated samples near the DP region show no significant change after annealing at 373 K and 473 K, but decrease significantly after annealing at 573 K, as displayed in Figures 3(b) and 4(b). This suggests that the quantity of vacancy and SIA defects generated by cascade collisions remains relatively stable after annealing at 373 K and 473 K, while decreasing substantially after annealing at 573 K. This substantial decrease is due to extensive recombination of vacancies and SIAs during annealing. Considering that an SIA in bcc iron has lower migration energy (0.17 eV [27]) than a vacancy (0.78 eV [28]), migration of numerous SIAs during annealing at 573 K dominates their recombination with vacancies. This result is consistent with DBS results for H^+-irradiated samples after annealing, where significant SIA migration occurs during annealing at 573 K. The recombination of abundant vacancies and SIAs after annealing at 573 K causes a significant decrease in S parameters and a notable increase in W parameters in the DP region, as shown in Figures 3(a) and 4(a).

Additionally, after annealing at 373 K, both S and W parameters near the DP region remain unchanged, indicating that 373 K annealing does not affect defects in the sample.

Strikingly, S parameters near the DP region for the H^+-irradiated sample increase significantly after annealing at 473 K, while W parameters remain constant. From DBS results, it appears that the amount of vacancy defects increases after annealing at 473 K while SIA defects remain unchanged. However, vacancies and SIAs typically occur in pairs, so an increase in vacancies should naturally accompany an increase in SIAs. Therefore, the observed rise in S parameters is not due to increased vacancies but rather to dissociation of hydrogen atoms from vacancies during annealing at 473 K. Research has demonstrated that hydrogen occupation in vacancies causes a decrease in the S parameter [29-30]. In other words, after H^+ irradiation, abundant hydrogen atoms were captured in vacancy defects formed near the DP region, resulting in vacancy-H complex formation. These complexes remain stable during annealing at 373 K but dissociate when annealing temperature is raised to 473 K, leading to increased S parameters.

Results from S-W plots at different annealing temperatures further indicate vacancy-H complex defect formation after H^+ irradiation. S-W plots are commonly used to assess defect types [31-33]. As shown in Figures 5(a) and (b), S-W plots for H^+-irradiated samples and those after annealing at 373 K and 473 K display "L" shapes, while the plot after annealing at 573 K displays a "Z" shape. Similarly, S-W plots for Ar^+-irradiated samples and those annealed at 373 K, 473 K, and 573 K all show "Z" shapes. These results suggest that defect types in the H^+-irradiated sample after 573 K annealing are the same as those in Ar^+-irradiated samples and their annealed counterparts, consisting of vacancy and SIA defects. In contrast, defect types in H^+-irradiated samples

and those annealed at 373 K and 473 K consist of vacancy-H complexes and SIA defects.

Due to its high diffusivity, hydrogen is difficult to retain in metals unless captured by defect traps. Simulation results indicate that the migration energy of hydrogen atoms in α-Fe is only 0.01 eV [34]. However, vacancies are effective traps for hydrogen atoms. Simulation studies have shown that hydrogen atoms are easily captured by vacancies in α-Fe, forming relatively stable vacancy-H complexes [35-36]. Experimentally, Clowers et al. used electron energy loss spectroscopy elemental mapping to characterize hydrogen capture in vacancies during Fe^+ irradiation of RAFM steel with hydrogen presence [6].

The first-principles calculation results in this study further provide insights into the mechanism by which hydrogen capture in vacancies affects irradiation defect formation. These results suggest that hydrogen capture in vacancies is a key factor in its significant promotion of irradiation defect formation. The mechanism is as follows: hydrogen occupying vacancies inhibits vacancy-SIA recombination, but this effect likely occurs only at higher hydrogen concentrations. First-principles calculations show this inhibitory effect only occurs when the number of hydrogen atoms in a vacancy reaches 5, as shown in Figure 6. Therefore, when high concentrations of hydrogen atoms are present during cascade collisions, vacancy-SIA recombination is inhibited, resulting in more vacancies and SIAs that contribute to defect formation.

5. Conclusion

In this study, positron annihilation DBS was used to characterize defect evolution in RAFM steel irradiated with H^+ and Ar^+, as well as in irradiated samples that underwent annealing at 373 K, 473 K, and 573 K. First-principles calculations were also employed to gain further insights into the synergistic effects of hydrogen and displacement damage on irradiation defect formation. The main conclusions are as follows:

(1) The peak damage doses for H^+ and Ar^+ irradiation are 0.2 dpa and 1 dpa, respectively. However, in the DP region, S parameters of the H^+-irradiated sample were comparable to those of the Ar^+-irradiated sample, while W parameters were smaller. Furthermore, S parameters of the H^+-irradiated sample after annealing at 473 K were even larger than those of the Ar^+-irradiated sample. These results indicate that hydrogen significantly promotes defect formation in the cascade collision region.

(2) Compared to the as-irradiated H^+ sample, S and W parameters show no significant changes near the DP region after annealing at 373 K. However, after annealing at 473 K, S parameters of the H^+-irradiated sample increase significantly near the DP region while W parameters remain unchanged. These results suggest that many hydrogen atoms are captured in vacancy defects near the DP region in the H^+-irradiated sample, forming vacancy-H complexes. First-principles calculations indicate that this

capture behavior contributes to hydrogen's promotion of defect formation. Specifically, when abundant hydrogen atoms occupy vacancies, recombination of vacancies and SIAs created in cascade collisions is inhibited.

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References

[1] R.L. Klueh, D.S. Gelles, S. Jitsukawa, A. Kimura, G.R. Odette, B. van der Schaaf, M. Victoria, Ferritic/martensitic steels-overview of recent results, Journal of Nuclear Materials 307-311 (2002) 455-465.
[2] N. Baluc, R. Schäublin, P. Spätig, M. Victoria, On the potentiality of using ferritic/martensitic steels as structural materials for fusion reactors, Nuclear Fusion 44 (2004) 56-61.
[3] S.J. Zinkle, J.T. Busby, Structural materials for fission & fusion energy, Materials Today 12 (2009) 12-19.
[4] G.D. Tolstolutskaya, V. V. Ruzhytskiy, I.E. Kopanets, S.A. Karpov, V. V. Bryk, V.N. Voyevodin, F.A. Garner, Displacement and helium-induced enhancement of hydrogen and deuterium retention in ion-irradiated 18Cr10NiTi stainless steel, Journal of Nuclear Materials 356 (2006) 136-147.
[5] J. Marian, T. Hoang, M. Fluss, L.L. Hsiung, A review of helium-hydrogen synergistic effects in radiation damage observed in fusion energy steels and an interaction model to guide future understanding, Journal of Nuclear Materials 462 (2015) 409-421.
[6] L.N. Clowers, Z. Jiao, G.S. Was, Synergies between H, He and radiation damage in dual and triple ion irradiation of candidate fusion blanket materials, Journal of Nuclear Materials 565 (2022) 153722.
[7] E. Wakai, T. Sawai, K. Furuya, A. Naito, T. Aruga, K. Kikuchi, S. Yamashita, S. Ohnuki, S. Yamamoto, H. Naramoto, S. Jistukawa, Effect of triple ion beams in ferritic/martensitic steel on swelling behavior, Journal of Nuclear Materials 307-311 (2002) 278-282.
[8] E. Wakai, K. Kikuchi, S. Yamamoto, T. Aruga, M. Ando, H. Tanigawa, T. Taguchi, T. Sawai, K. Oka, S. Ohnuki, Swelling behavior of F82H steel irradiated by triple/dual ion beams, Journal of Nuclear Materials 318 (2003) 267-273.
[9] T. Tanaka, K. Oka, S. Ohnuki, S. Yamashita, T. Suda, S. Watanabe, E. Wakai, Synergistic effect of helium and hydrogen for defect evolution under multi-ion irradiation of Fe-Cr ferritic alloys, Journal of Nuclear Materials 329-333 (2004) 1138-1142.

[10] O. V. Borodin, V. V. Bryk, A.S. Kalchenko, V. V. Melnichenko, V.N. Voyevodin, F.A. Garner, Synergistic effects of helium and hydrogen on self-ion-induced swelling of austenitic 18Cr10NiTi stainless steel, Journal of Nuclear Materials 442 (2013) S817-S820.
[11] Y.E. Kupriiyanova, V. V. Bryk, O. V. Borodin, A.S. Kalchenko, V.N. Voyevodin, G.D. Tolstolutskaya, F.A. Garner, Use of double and triple-ion irradiation to study the influence of high levels of helium and hydrogen on void swelling of 8-12% Cr ferritic-martensitic steels, Journal of Nuclear Materials 468 (2016) 264-273.
[12] L. Jiang, Q. Peng, P. Xiu, Y. Yan, Z. Jiao, C. Lu, T. Liu, C. Ye, R. Shu, Y. Liao, Q. Ren, F. Gao, L. Wang, Elucidating He-H assisted cavity evolution in alpha Cr under multiple ion beam irradiation, Scripta Materialia 187 (2020) 291-295.
[13] F.A. Selim, Positron annihilation spectroscopy of defects in nuclear and irradiated materials- a review, Materials Characterization 174 (2021) 110952.
[14] Q. Huang, Status and improvement of CLAM for nuclear application, Nuclear Fusion 57 (2017) 086042.
[15] Standard Practice for Neutron Radiation Damage Smulation by Charged-particle Irradiation, ASTM Designation E 521-89, Annual Book of ASTM Standards, vol. 12.02, American Society for Testing and Materials, Philadelphia, PA, 1989, p. D-9.
[16] M.K. Teng, D.X. Shen, Y.F. Xia., Positron Annihilation Spectroscopy and Application, Atomic Energy Press, Beijing, (2000) 4-6.
[17] G. Kresse, J. Furthmüller, Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set, Physical Review 54 (1996) 11169.
[18] C.C. Fu, F. Willaime, Ab initio study of helium in α-Fe: Dissolution, migration, and clustering with vacancies, Physical Review B 72 (2005) 064117.
[19] G. Kresse, J. Hafner, Ab initio molecular dynamics for liquid metals, Physical Review B 47 (1992) 558-561.
[20] J.P. Perdew, J.A. Chevary, S.H. Vosko, K.A. Jackson, M.R. Pederson, D.J. Singh, C. Fiolhais, Erratum: Atoms, molecules, solids, and surfaces: Applications of the generalized gradient approximation for exchange and correlation, Physical Review B 48 (1993) 4978.
[21] D.T. Britton, P.C. Rice-Evans, J.H. Evans, Positron annihilation study of the temperature behaviour of solid krypton deposits in copper, Philosophical Magazine A 55 (1987) 347-357.
[22] J. Qiu, Y. Xin, X. Ju, L.P. Guo, B.Y. Wang, Y.R. Zhong, Q.Y. Huang, Y.C. Wu, Investigation by slow positron beam of defects in CLAM steel induced by helium and hydrogen implantation, Nuclear Instruments and Methods in Physics Research B 267 (2009) 3162-3165.
[23] X. Gai, R. Smith, S.D. Kenny, Inert gas bubbles in bcc Fe, Journal of Nuclear Materials 470 (2016) 84-89.
[24] D.J. Bacon, A.F. Calder, F. Gao, Defect production due to displacement cascades in metals as revealed by computer simulation, Journal of Nuclear Materials 251 (1997) 255-260.

[25] E. Meslin, A. Barbu, L. Boulanger, B. Radiguet, P. Pareige, K. Arakawa, C.C. Fu, Cluster-dynamics modelling of defects in α-iron under cascade damage conditions, Journal of Nuclear Materials 382 (2008) 190-196.
[26] B. Michaut, T. Jourdan, J. Malaplate, A. Renault-Laborne, F. Sefta, B. Décamps, Cluster dynamics modeling and experimental investigation of the effect of injected interstitials, Journal of Nuclear Materials 496 (2017) 166-176.
[27] N. Soneda, T. Diaz de la Rubia, Migration kinetics of the self-interstitial atom and its clusters in bcc Fe, Philosophical Magazine A 81 (2001) 331-343.
[28] K. Sato, T. Yoshiie, T. Ishizaki, Q. Xu, Behavior of vacancies near edge dislocations in Ni and α-Fe: Positron annihilation experiments and rate theory calculations, Physical Review B 75 (2007) 094109.
[29] Q. Xu, K. Sato, X.Z. Cao, P. Zhang, B.Y. Wang, T. Yoshiie, H. Watanabe, N. Yoshida, Interaction of deuterium with vacancies induced by ion irradiation in W, Nuclear Instruments and Methods in Physics Research B 315 (2013) 146-148.
[30] X.L. Zhu, Y. Zhang, L. Cheng, Y. Yuan, G. De Temmerman, B.Y. Wang, X.Z. Cao, G.H. Lu, Deuterium occupation of vacancy-type defects in argon-damaged tungsten exposed to high flux and low energy deuterium plasma, Nuclear Fusion 56 (2016) 036010.
[31] Y.C. Wu, Y.C. Jean, Hydrogen damage in AISI 304 stainless steel studied by Doppler broadening, Applied Surface Science 252 (2006) 3278-3284.
[32] Q. Cao, X. Ju, L. Guo, B. Wang, Helium-implanted CLAM steel and evolutionary behavior of defects investigated by positron-annihilation spectroscopy, Fusion Engineering and Design 89 (2014) 1101-1106.
[33] E. Lu, X. Cao, S. Jin, P. Zhang, C. Zhang, J. Yang, Y. Wu, L. Guo, B. Wang, Investigation of vacancy-type defects in helium irradiated FeCrNi alloy by slow positron beam, Journal of Nuclear Materials 458 (2015) 240-244.
[34] V. V Kirsanov, M. V Musina, V. V Rybin, The influence of hydrogen on the formation of helium vacancy voids in metal, Journal of Nuclear Materals 191-194 (1992) 1318-1322.
[35] E. Hayward, C. Deo, Synergistic effects in hydrogen-helium bubbles, Journal of Physics: Condensed Matter 24 (2012) 265402.
[36] A.H.M. Krom, A.D. Bakker, Hydrogen Trapping Models in Steel, Metallurgical and Materials Transactions B 31 (2000) 1475-1482.

Note: Figure translations are in progress. See original paper for figures.