

Article

Microstructure Characterization and Hardening Evaluation of Ferrite/Martensitic Steels Induced by He²⁺ Irradiation

Guangjie Zhang ^{1,2} , Junfeng Yang ^{2,3,*} , Zhuoming Xie ², Linchao Zhang ², Rui Liu ², Meng Sun ² , Gang Li ⁴, Hui Wang ⁵, Yi Hu ^{1,2}, Xuebang Wu ², Qianfeng Fang ², Changsong Liu ² and Xianping Wang ^{2,*}

¹ Department of Materials Science and Engineering, University of Science and Technology of China, Hefei 230026, China

² Key Laboratory of Materials Physics, Institute of Solid State Physics, Hefei Institutes of Physical Science, Chinese Academy of Sciences, Hefei 230031, China

³ Lu'an Branch, Anhui Institute of Innovation for Industrial Technology, Lu'an 237100, China

⁴ Science and Technology on Reactor Fuel and Materials Laboratory, Nuclear Power Institute of China, Chengdu 610041, China

⁵ School of Mechanical Engineering, Chengdu University, Chengdu 610106, China

* Correspondence: jfyang@issp.ac.cn (J.Y.); xpwang@issp.ac.cn (X.W.)

Abstract: Two ferrite/martensitic (F/M) steels with different Si concentrations (0 and 0.4 wt.%) were irradiated by 250 keV He²⁺ ions with different fluences of 2×10^{16} ions/cm² and 1×10^{17} ions/cm². Transmission electron microscopy and a nanoindenter were employed to investigate their microstructure evolution and irradiation hardening effects induced by high-energy He²⁺ ions. A large number of He bubbles formed in the Si-free and Si-containing F/M steels, which preferentially nucleated and grew at the lath and phase boundaries. Owing to the inhibiting effect of Si addition on He bubble growth, the He bubbles in the Si-containing sample exhibited smaller size and higher density at the same He²⁺ fluence. Nanoindenter measurement revealed that typical irradiation hardening was observed in the F/M steel, and 1/2<111> and <100> type dislocation loops formed by He²⁺ irradiation was recognized as the dominant mechanism. The addition of Si induced an increase in the number density of dislocation loops, leading to the exacerbation of the irradiation hardening, and the results are basically in agreement with the theoretical analysis based on the dispersion barrier hardening (DBH) and Friedel–Kroupa–Hirsch (FKH) models.

Keywords: ferrite/martensitic steel; He bubble; dislocation loop; irradiation hardening



Citation: Zhang, G.; Yang, J.; Xie, Z.; Zhang, L.; Liu, R.; Sun, M.; Li, G.; Wang, H.; Hu, Y.; Wu, X.; et al.

Microstructure Characterization and Hardening Evaluation of Ferrite/Martensitic Steels Induced by He²⁺ Irradiation. *Crystals* **2023**, *13*, 1308. <https://doi.org/10.3390/cryst13091308>

Academic Editor: Qing-Qiang Ren

Received: 8 August 2023

Revised: 17 August 2023

Accepted: 21 August 2023

Published: 27 August 2023



Copyright: © 2023 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).

1. Introduction

Ferrite/martensitic (F/M) steels are of increasing interest and have prospective applications as structural materials in the field of nuclear reactors owing to their superior thermal conductivity, thermal expansion, and resistance to helium radiation-induced swelling and embrittlement [1–3]. In fusion or fission reactors like lead-cooled fast reactors (LFR), structural materials will be directly exposed to more severe service environments than existing commercial fission reactors, such as liquid lead–bismuth eutectic (LBE) corrosion, high temperatures (about 500–550 °C), and high neutron irradiation (50–150 dpa) [4]. Therefore, it is important for the use of F/M steels in LFR to take into account the resistance to irradiation embrittlement and irradiation swelling, LBE dissolution corrosion and corrosion embrittlement, besides the excellent high-temperature mechanical properties, including high strength and good elongation.

The corrosion of F/M steel by LBE could lead to surface modification through the formation, thickening and shedding of the oxide layer [5,6], thus deteriorating its mechanical properties. It has been reported that the addition of Si to the matrix can not only improve the mechanical properties of F/M steel by solid solution strengthening and promoting precipitation [7] but also enhance its corrosion resistance by forming a protective oxide film

on the surface [8]. It is necessary to point out that excess Si can easily result in an increase in high-temperature ferrite and Laves phases, and therefore lead to an obvious decrease in mechanical properties, especially under irradiation conditions. Dvoriashin et al. [2] investigated the degradation of mechanical properties of F/M steels with different Si contents after irradiation, and the results showed that F/M steels with Si contents in the range of 0.18 wt.%~1.05 wt.% could maintain good mechanical properties after irradiation at 490 °C/50 dpa, while once the Si content reached or exceeded 1.9 wt.%, significant irradiation hardening and irradiation embrittlement were observed. A similar phenomenon was also found by Porollo et al. [9]. Based on these considerations, it is very important to find a suitable Si content range in F/M steel in order to synergistically optimize its corrosion resistance and mechanical properties.

Besides corrosion effects, high temperatures generally deteriorate the high-temperature creep and properties of structural materials by changing their microstructure through a long aging process, including the coarsening of MX and $M_{23}C_6$ precipitates and martensitic laths [10–12], and the formation of brittle Laves phases [13], which easily leads to brittle fracture of F/M steel. In addition, the displacement damage effect under the irradiation environment [14–16] is also an important factor leading to the degradation of material properties. It was reported that high-flux fission neutrons not only cause displacement cascades of atoms to form vacancies, clusters, interstitial atoms, and other point defects but also lead to the generation of a new element He because of (n, α) transmutation reactions. Since He is almost insoluble in steel and easily migrates in F/M steel, this makes it difficult to dissolve once it is formed [17]. Moreover, He atoms can be trapped by different kinds of boundaries (grain/subgrain, martensite pocket/block/lath, and precipitates, etc.) [18], dislocations and other sinks in the F/M steel to form a He cluster [19,20]. The formed He cluster continuously absorbs external He atoms, eventually leading to the generation of a high density of He bubbles, as observed by transmission electron microscopy (TEM) [21]. The formed He bubbles are considered to be one of the main causes of the mechanical performance deterioration of F/M steel.

Temperature is another important factor related to the irradiation resistance of materials, especially for the formation of dislocation [22]. It was reported [23] that when pure iron was irradiated at 400 °C or below, non-edge dislocation loops of interstitial nature with Burgers vectors $b = 1/2\langle 111 \rangle$ were produced predominantly, while when the irradiated temperature reached 500 °C or above, only $b = \langle 100 \rangle$ type pure-edge dislocation loops were formed. As is known, BCC metals generally have a high work-hardening rate, which made it relatively easy to achieve considerable strength and hardness due to the poor movability [23,24] of the screw dislocations below the critical temperature (340 K for α -Fe [25,26]).

To further understand the influence of Si concentration on mechanical properties, and irradiation resistance, series Si-containing F/M steels (0~1.0 wt.% Si) were newly developed by the Nuclear Power Institute of China for potential application in LFR, and the reported results showed that the developed F/M steel exhibited good corrosion resistance and comprehensive mechanical properties in the case of 0.4 wt.% Si addition. However, whether it can account for irradiation resistance needs to be further studied [27,28]. Yang Chen et al. [29] reported the behavior of an Fe9Cr1.5W0.4Si alloy irradiated with helium ions at low energy and low dose, and Yiheng Chen et al. [10] studied the irradiation behavior of steels with different Si content that were irradiated with iron ions at high energy and high dose, but there are fewer studies on medium-energy and medium- or low-dose irradiation. In addition, as discussed earlier, the effect of helium ion irradiation on dislocation loops in these newly developed F/M steels has rarely been reported.

In this investigation, two F/M steels with different Si concentrations (0, 0.4 wt.% Si) were irradiated by He^{2+} ion irradiation at 400 °C and below in order to understand the effects of He^{2+} irradiation on dislocation loops in these newly developed F/M steels, and the typical irradiation hardening was observed and discussed based on the microstructure and nanoindentation analysis.

2. Experiment

Two F/M steel samples with different silicon contents were provided by the Nuclear Power Institute of China. They were normalized at 1020 °C for 1 h followed by water-quenching, tempering at 700 °C for 1.5 h and air cooling. The chemical compositions of the two samples are listed in Table 1.

Table 1. Chemical composition of two F/M steel samples (wt.%).

Sample	C	Cr	W	Mn	V	Ta	Zr	Si	Fe
0Si	0.091	9.1	1.52	0.57	0.19	0.094	<0.002	0.022	Bal.
0.4Si	0.095	9.05	1.53	0.59	0.19	0.082	<0.002	0.37	Bal.

Before the He^{2+} irradiation experiments, the two different Si-containing F/M steel sheets (0Si and 0.4Si) were cut into $3 \times 3 \times 1 \text{ mm}^3$ squares and then ground with 2000 grit sandpaper, followed by mechanical chemical polishing to remove the surface stress [30] of the samples. Then the irradiation experiment was carried out at an irradiation terminal of 320 kV high-voltage platform in the Institute of Modern Physics in Lanzhou, China. The stress-free samples were implanted with 250 keV He^{2+} under $7 \times 10^{-5} \text{ Pa}$ at room temperature (RT, about 25 °C) and 400 °C, respectively. To investigate the effects of displacement damage on F/M steel, two different He^{2+} fluences of 2×10^{16} and $1 \times 10^{17} \text{ ions/cm}^2$ were chosen.

The irradiation damage and He concentration distribution with implantation depth of two different matrices (Fe9Cr1.5W and Fe9Cr1.5W0.4Si) were simulated by the SRIM 2008 program. During the simulation process, the Detailed Calculation with full Damage Cascades mode was chosen, in which the threshold energy for Fe, Cr, W and Si was 40, 40, 90 and 35 eV, respectively. Figure 1 shows the SRIM simulation RT. The maximum irradiation damage of the Fe9Cr1.5W (0Si steel) induced by He^{2+} was up to 0.82 and 4.11 dpa, which corresponds to two different He^{2+} fluences of 2×10^{16} and $1 \times 10^{17} \text{ ions/cm}^2$, respectively. As for He distribution, a relatively sharp peak extending from 600 to 1200 nm was observed, and the He peaks in depth were both 1005 nm for the lower and higher He^{2+} fluences, respectively. The maximum implantation depth of He was about 1250 nm which was independent of He fluences. In Figure 1b, the peak value of irradiation damage and He distribution for the Fe9Cr1.5W0.4Si (0.4Si steel) sample are seen to exhibit a similar characteristic to that in the Si-free sample.

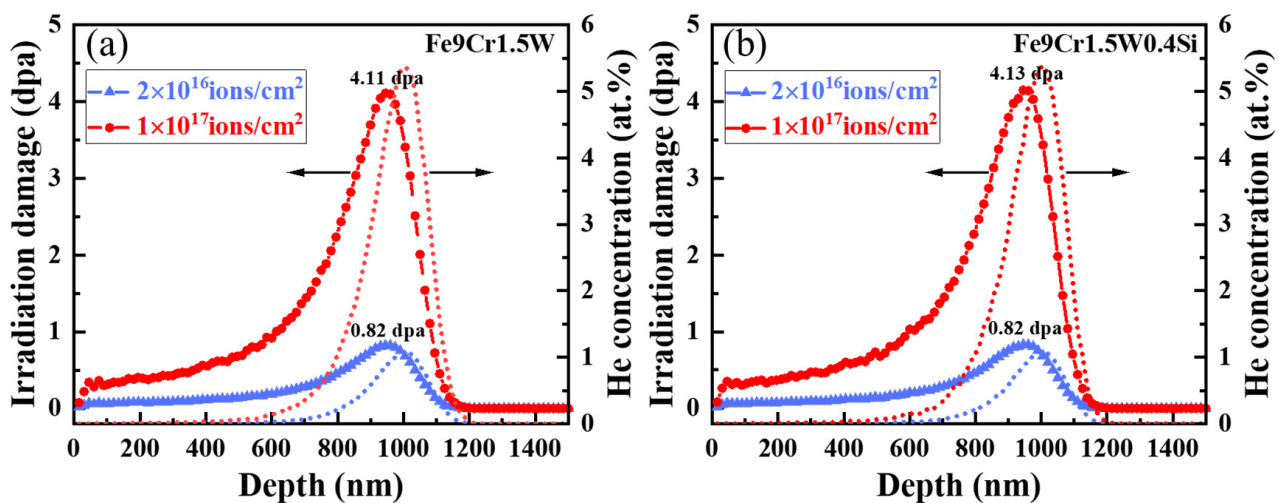


Figure 1. Variation of irradiation damage and He concentration with depth calculated by SRIM for (a) Fe9Cr1.5W and (b) Fe9Cr1.5W0.4Si steel.

The microstructure of the two F/M steels with different Si concentrations before irradiation was characterized by transmission electron microscope (TEM, Tecnai G2 F20). For TEM observation, several $\Phi 3$ mm discs were successively ground to about 50–70 μm with 240, 800, 1500, and 2000 grit sandpaper, then electrochemically polished using a 10% ethanol perchlorate solution by a Struers Tenupol-5 twinjet electro-polisher, where the voltage and temperature was 25 V and -20 $^{\circ}\text{C}$, respectively. To characterize the microstructure of the irradiated samples, TEM samples with a thickness of about 100 nm were prepared by Helios 5's focused ion beam (FIB). The helium bubbles and dislocation loops were manually counted in Nanomeasurer software using images obtained by TEM. The mechanical properties of the irradiated samples were measured by a nanoindenter (Nano Indenter G200, Agilent Corp., Santa Clara, CA, USA), in which 16 indentations were tested and averaged on each sample to minimize the measurement error of hardness as far as possible. The test mode was continuous stiffness measurement (CSM) with a maximum depth of 2000 nm.

3. Results and Discussion

3.1. Microstructure of Different Steels before Irradiation

The microstructure of the unirradiated samples characterized by high-resolution TEM analysis is shown in Figure 2, and typical martensitic laths and high-density dislocations (about $2.56 \times 10^{14}/\text{m}^2$ measured by X-ray diffraction [31,32] method) are observed in the two F/M samples. Moreover, two types of precipitates exist at the martensitic lath boundary and within the martensite phase, and our previous EDS results (Figure 2c) verified that the rod-like particle is a Cr, Mn, W-rich M_{23}C_6 phase, while the spherical particle is an MX phase rich in Ta and V [1,33].

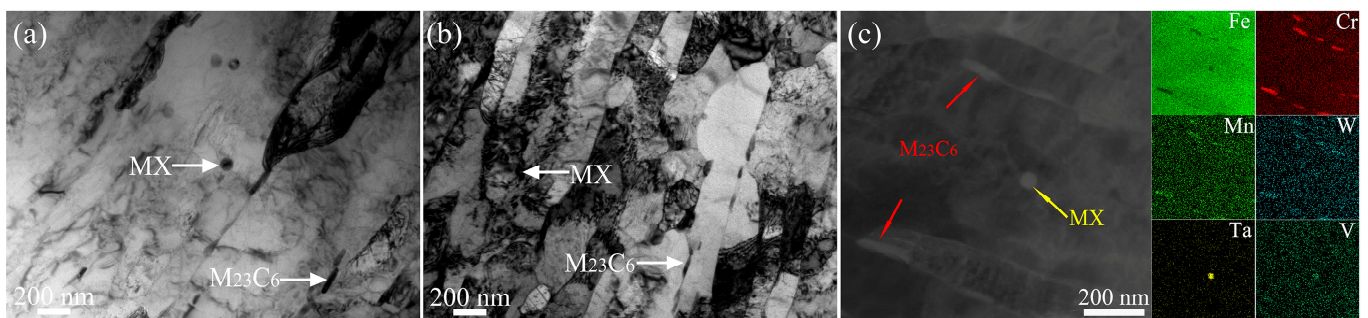


Figure 2. TEM images of non-irradiated (a) 0Si steel, (b) 0.4Si steel, and (c) left: HAADF image of 0.4Si steel, right: EDS mappings of the left HAADF image.

3.2. Microstructure of Different Steels after Irradiation

The microstructure evolution of the two F/M steels after high-fluence (1×10^{17} ions/ cm^2) He^{2+} irradiation at RT is shown in Figure 3. As shown in Figure 3a,b, irradiation damage bands with different contrasts to the matrix were formed regardless of the silicon content; this phenomenon corresponds to the vicinity of the peak in the irradiation damage region simulated by SRIM. Many small white-circled He bubbles appeared at lath or subgrain and precipitate boundaries, indicating that these interfaces can effectively trap He to promote the formation of He bubbles, as reported in ref. [34]. The He bubble sizes produced by irradiation for the two investigated samples are about 1.5 nm (Figure 3c,d), which is almost independent of the Si level in the F/M matrix.

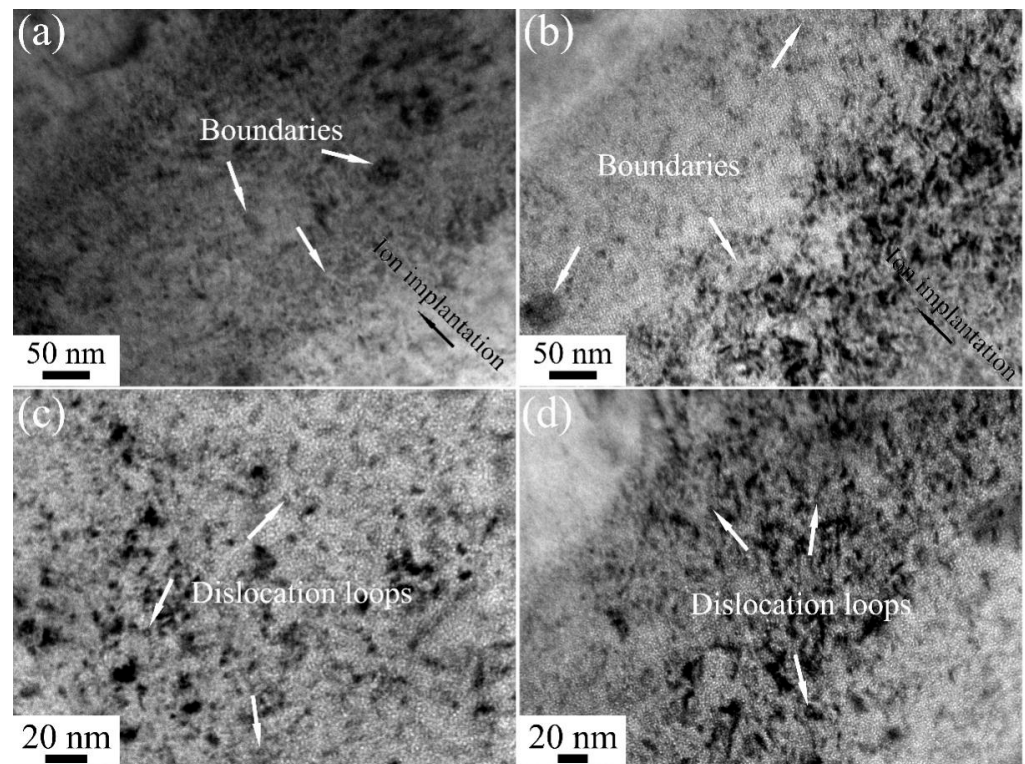


Figure 3. Microstructure of (a,c) 0Si, (b,d) 0.4Si steels after irradiation at RT with a fluence of 1×10^{17} ions/cm².

As is known, temperature is a key factor for He bubble growth in metal. The reason is that the nucleated He bubble tends to absorb the surrounding He atoms and grow gradually as the irradiation temperature increases [34]. To further understand the relation of He bubble growth to irradiation temperature in different Si-containing F/M steels, Figure 4a,c give the TEM images of the He bubbles in the 0Si and 0.4Si F/M steels after irradiation at 400 °C, respectively, and the implanted He²⁺ fluence controlled at a value of 1×10^{17} ions/cm². It is shown that the He bubble size obviously increased with the increasing irradiation temperature, from about 1.5 nm (Figures 3c,d and 5a,b) at RT to more than 4.3 nm (Figure 5c) and 3.9 nm (Figure 5d) at 400 °C for the Si-free and Si-containing samples, respectively, but the helium bubble density produced by irradiation at 400 °C decreased compared to that at RT. From the thermodynamic point of view, according to the Arrhenius equation, the diffusion capacity (D) of the defects can be expressed as:

$$D = Ae^{-\frac{Q}{k_B T}}, \quad (1)$$

where A , Q , k_B and T are the pre-exponential factor, activation energy, Boltzmann constant, and temperature, respectively. From Equation (1), as the temperature increases, the diffusion capacity of defects such as helium atoms will also increase; thus, the helium bubble nucleus can continuously absorb helium atoms, causing its volume to grow and density to decrease. In Table 2, the quantitative statistics of the size and number density of helium bubbles at different fluences of 400 °C are presented in detail. Besides the effects of He²⁺ fluence, it is worth noting that, in the 0.4Si sample, the smaller helium bubble size and the larger helium bubble density are observed in comparison with the Si-free sample under the same irradiation temperature, which reveals that the addition of 0.4 wt.% Si has typical inhibiting effects on the growth of the He bubble. In other words, 0.4Si F/M steel has an advantage over the Si-free sample in terms of resistance to irradiation swelling, which provides a potential reference idea in the design of high-performance anti-irradiation materials.

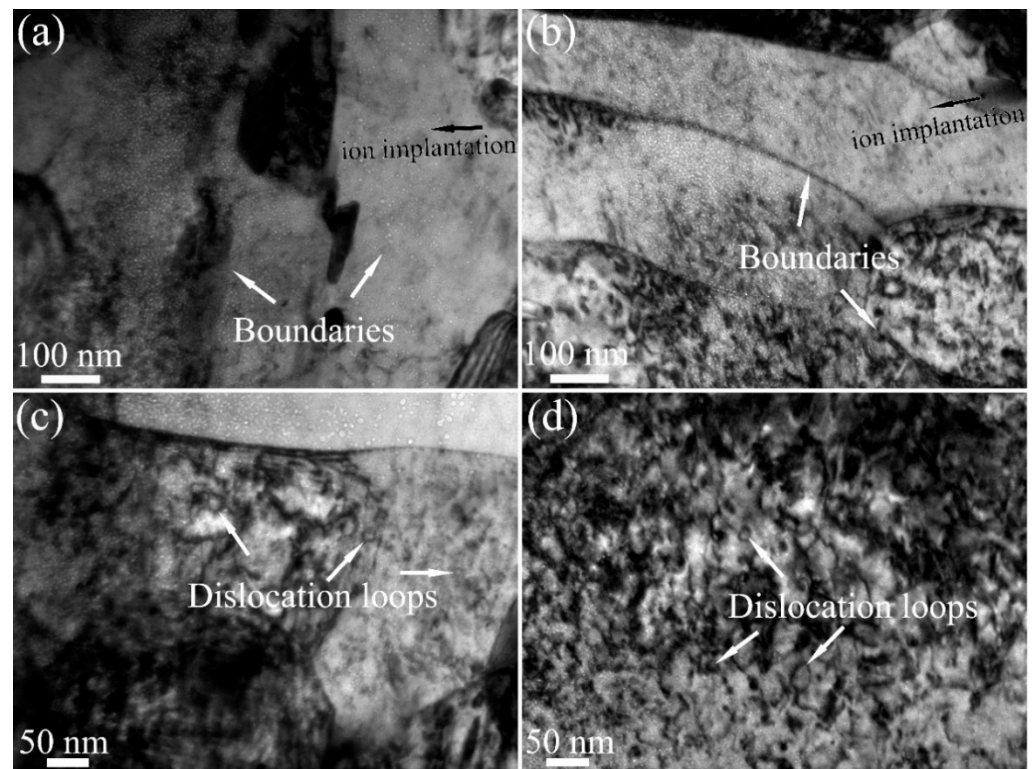


Figure 4. Microstructure of (a,c) 0Si, and (b,d) 0.4Si steels after irradiation at 400 °C with a fluence of 1×10^{17} ions/cm².

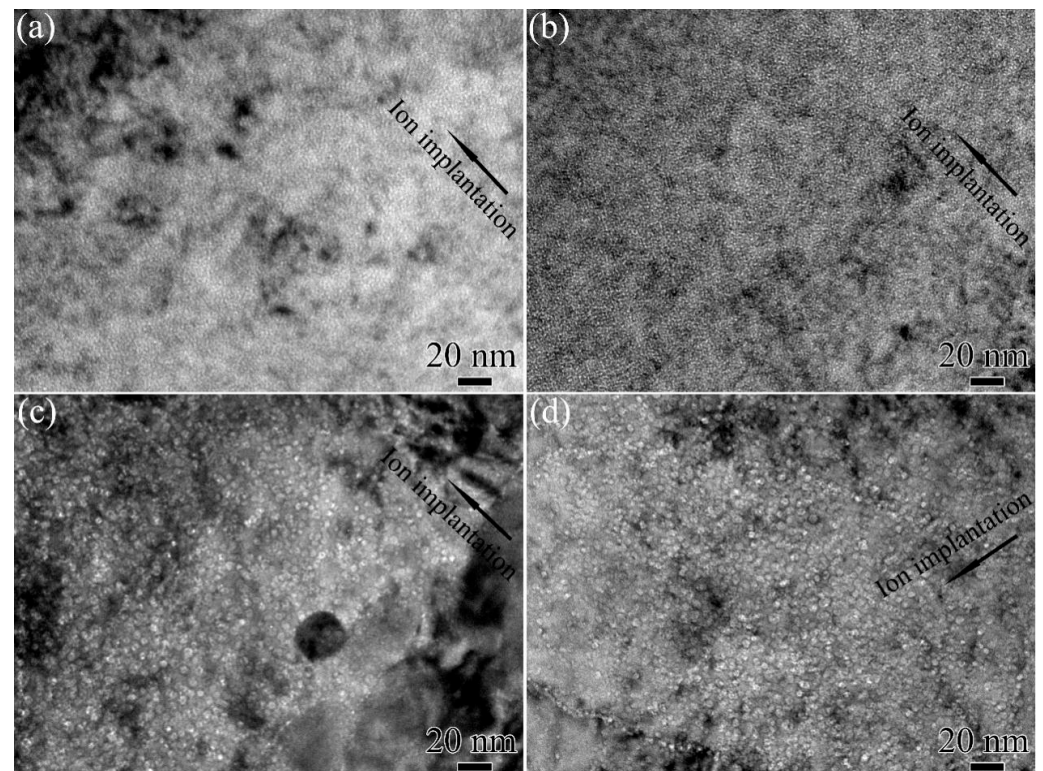


Figure 5. Helium bubble morphology of (a,c) 0Si and (b,d) 0.4Si steels irradiated at (a,b) room temperature and (c,d) 400 °C with a fluence of 1×10^{17} ions/cm².

Table 2. Mean diameter and number density of He bubbles and dislocation loops of 0Si and 0.4Si steels when irradiated at 400 °C.

Composition	Fluence (Ions/cm ²)	Mean Size (nm)		Number Density (×10 ²² /m ³)	
		He Bubble	Loops	He Bubble	Loops
0Si	2 × 10 ¹⁶	2.9	17.6	4.0	0.08
	1 × 10 ¹⁷	4.3	17.8	2.4	0.25
0.4Si	2 × 10 ¹⁶	2.6	16.4	4.4	0.31
	1 × 10 ¹⁷	3.9	18.8	4.1	0.38

Dislocation is also another effective deficiency trap for the absorption of He atoms and other impurities. For He²⁺ irradiation at RT and 400 °C, the dislocation loop morphologies of the F/M samples with different Si contents are given in Figure 3c,d and Figure 4c,d. It can be seen that the number density of dislocation loops tends to increase in the condition of Si addition regardless of irradiation temperature, as shown in Table 2, which is consistent with the subsequent irradiation hardening phenomenon in different Si-containing F/M samples.

3.3. Mechanical Properties before and after Irradiation

Figure 6 displays the mechanical properties of steels with different silicon content before and after irradiation as evaluated by nano-indentation. As shown for the two F/M samples under different irradiation temperatures and He fluence, all the obtained indentation depth curves with nano-hardness can be divided into three stages: the reverse indentation size effect (RISE) stage, the indentation size effect (ISE) stage and the soft substrate effect (SSE) stage. The RISE stage generally corresponds mainly to the depth region less than 100 nm from the sample surface [35,36], while for the ISE stage, the value of nano-hardness closely varies depending on the material composition and irradiation temperature, but hardly changes with He fluence. According to the model of geometrically necessary dislocations, the smaller the ISE stage, the greater the defects in densities and the hardness [37]. In the ISE stage for different Si-containing F/M samples, the covered indentation range is obviously different with increasing Si concentrations, and shrinks from 100–372 nm (Figure 6a) and 100–427 nm (Figure 6c) in the 0Si sample to 100–348 nm (Figure 6b) and 100–382 nm (Figure 6d) in the 0.4Si sample when irradiated at RT and 400 °C, respectively. These results indicate that the addition of silicon in F/M steels can effectively reduce the influence of the unirradiated soft substrate on the hardness of the irradiated zone. In other words, the irradiation hardening will increase with the increase in Si content in F/M steel, but decrease with the increase in irradiation temperature under the same Si composition. The region beyond the ISE stage belongs to the SSE stage, which changes accordingly with the ISE stage.

Considering the microstructure evolution, the He²⁺ irradiation generally forms high-concentration He bubbles, dislocation loops and other irradiation defects in the matrix of F/M steel, which is the key factor in irradiation hardening. To further evaluate the degree of irradiation hardening caused by He²⁺ irradiation in different Si-containing F/M steel, the Nix-Gao model [38] based on the concept of geometrically necessary dislocations is used, which is given as follows:

$$H^2 = H_0^2 + H_0^2 h^* \frac{1}{h}, \quad (2)$$

where H is the hardness value at a particular indentation depth (h), and H_0 is the hardness limited to infinity (i.e., bulk-equivalent hardness) which can be applied to assess the irradiation hardening effect in the irradiated F/M steels due to the excludability of the size effect, and h^* is a characteristic length that depends on the shape of the indenter. Based on Equation (2) above, the original hardness depth curve can be transferred to an H^2 versus $1/h$ curve, as shown in Figure 7. It is shown that the linear fitting results of the H^2 versus $1/h$ for the two unirradiated steels are feasible in the depth range from 125 nm to 2000 nm, but, in

the irradiated cases, an obvious linear deviation is observed near the dividing line between the ISE and SSE stages, similar to the reported results in ref. [34]. This result indicates that the ISE region plays a key role in the irradiation hardening mechanism of F/M steel. Based on this consideration, a linear fitting only limited in the ISE stage is needed to accurately obtain the value of H_0 that reflects the hardness of the irradiated material.

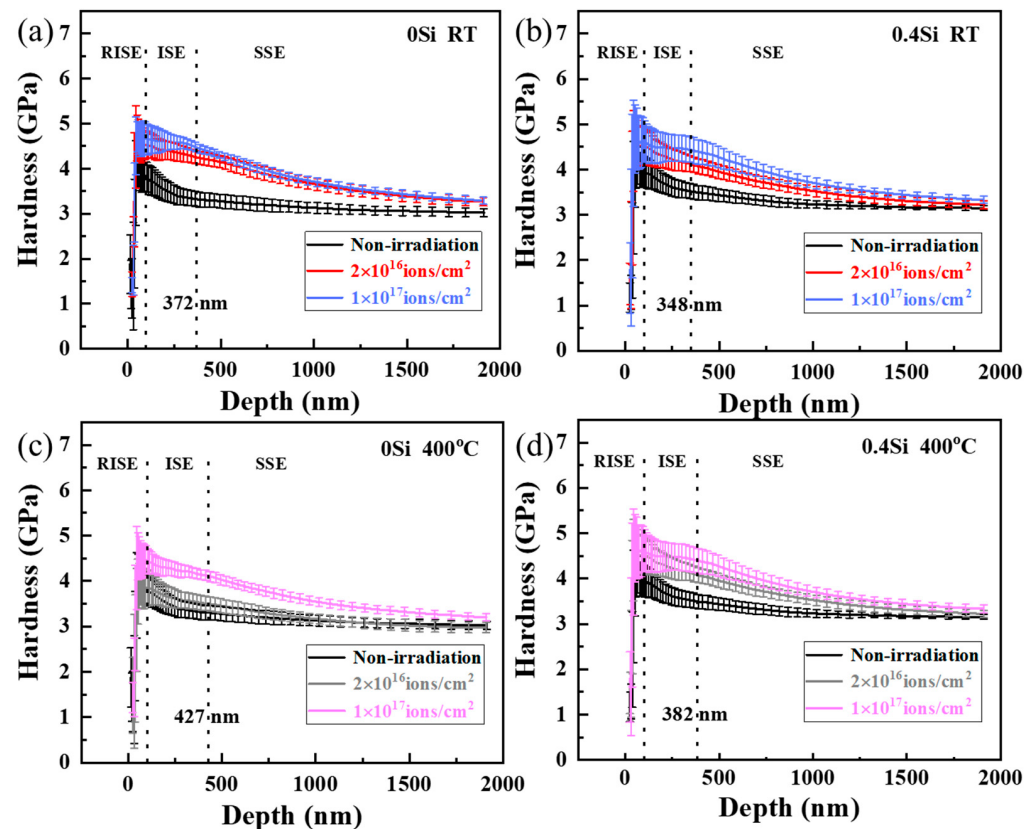


Figure 6. The nano-hardness (H) versus depth (h) for (a,c) 0Si and (b,d) 0.4Si steels irradiated at RT and 400 °C with different implantation fluences, respectively.

Based on the linear fitting results in the ISE region, the detailed values of H_0 for 0Si and 0.4Si steels at different irradiation temperatures and fluences are listed in Table 3. As shown in Table 3, the H_0 value of the unirradiated F/M steel slightly increases with increasing Si content, from 3.1 GPa for 0Si steel to about 3.2 GPa for 0.4Si steel. In our previous investigation [39], different factors affecting each strengthening mechanism in F/M steel, including the size, number density and area fraction of the precipitates, the width of the martensite laths and dislocation density, and the Si addition as well, have been carefully investigated, and the main contribution was ascribed to the solid solution strengthening induced by Si addition.

Table 3. The values of H_0 for 0Si and 0.4Si steels under different irradiation conditions.

Irradiation Condition		0Si	0.4Si
RT	Non-irradiated	3.1	3.2
	2×10^{16} ions/cm ²	4.2	4.4
	1×10^{17} ions/cm ²	4.5	5.0
	2×10^{16} ions/cm ²	3.4	4.0
	1×10^{17} ions/cm ²	4.0	4.3

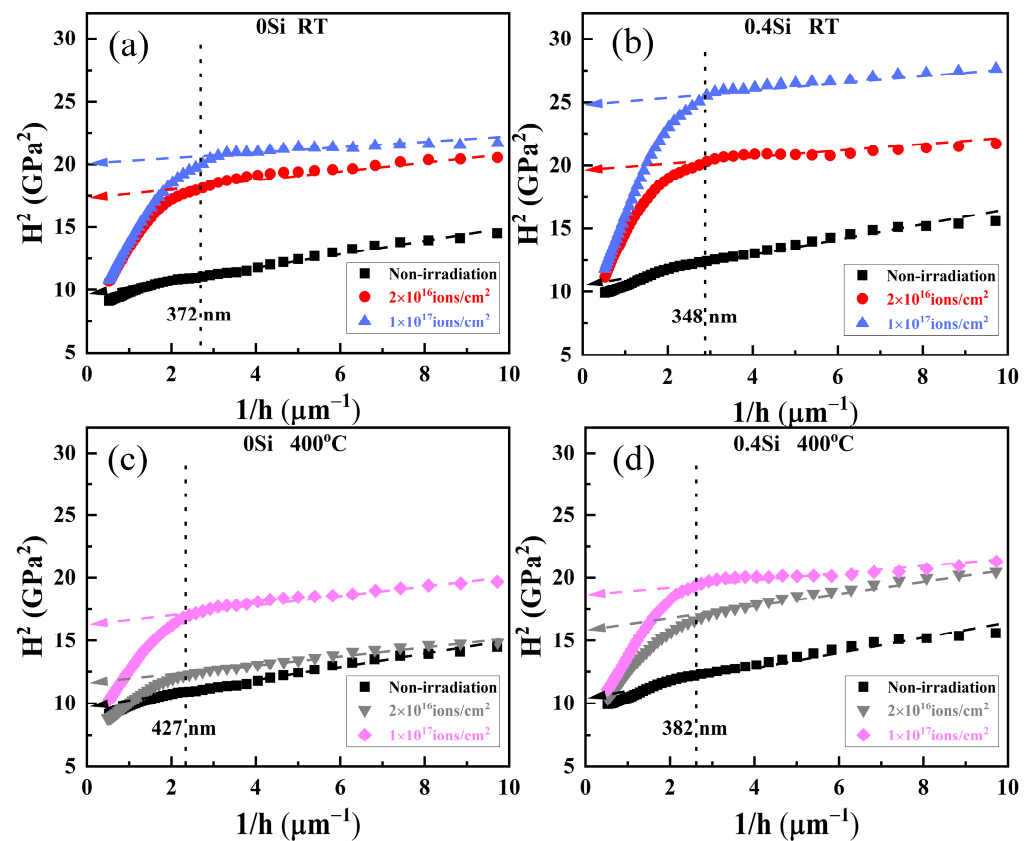


Figure 7. The profile of H^2 versus $1/h$ for (a,c) 0Si and (b,d) 0.4Si steels irradiated at RT and 400 °C with different implantation fluences, respectively.

As for the hardness variation after He^{2+} irradiation, typical irradiation hardening phenomena are observed due to the formation of He bubbles and dislocation loops in the matrix of the F/M steels, as shown in Figures 3 and 4. As noted from Table 3, besides the effects of Si level, temperature and fluence are also closely related with induced hardening of He^{2+} irradiation, namely, the hardening value increases with He fluence but decreases with irradiation temperature under the same Si composition. With increasing He fluence, higher density He bubbles and dislocation loops will be formed and therefore result in the increase in H_0 . On the contrary, the enhancement of the irradiation temperature will inevitably promote the diffusion of He atoms and the annihilation of dislocation loops, and leads to a decrease in their density [34], accordingly resulting in a decrease in irradiation hardening. The contribution of He bubbles to irradiation hardening can be expressed by the Friedel–Kroupa–Hirsch (FKH) model [40] as follows:

$$\Delta\sigma_{\text{bubble}} = \frac{1}{8} M \mu b d N^{\frac{2}{3}}, \quad (3)$$

$$\Delta H = 3\sigma_y, \quad (4)$$

where $M = 3.06$ is the Taylor factor for BCC metals, $\mu = 71.85$ GPa is the shear modulus for F/M steel [41], $b = 0.248$ nm is the Burgers vector [10], d and N are the mean diameter and number density of He bubbles, respectively. Taking the 400 °C irradiation sample as an example, the mean diameter and number density of He bubbles were counted and listed in Table 2, and thus the contributions of He bubbles to the yield strength were calculated by Equation (3) to be 0.023, 0.024, 0.022 and 0.032 GPa for a low and high fluence of 0Si and 0.4Si, and the corresponding ΔH_{bubble} were 0.069, 0.072, 0.066 and 0.096 GPa,

respectively, implying that silicon has little effect on the irradiation hardening caused by He bubbles.

In the analysis of irradiation hardening, dislocation is generally recognized as one of the important factors; different types of dislocation loops make different strengthening contributions in F/M steels owing to the difference in mobility. To further understand the mechanisms of dislocation loops on irradiation hardening in F/M steel, it is necessary to characterize the types of dislocation loops based on g-vector imaging. In Figure 8 the TEM images of 0.4Si steel irradiated at 400 °C with a fluence of 2×10^{16} ions/cm² are shown as an example in particular. The dislocation loops in the F/M matrix were characterized under the same zone axis of $z = [001]$ but different g vectors of $[020]$, $[\bar{1}10]$, $[\bar{2}00]$, $[110]$. Based on the corresponding extinction conditions listed in Table 4, the Burgers vectors of dislocation loops are highlighted in different colors. As shown in Figure 8, there are at least three kinds of dislocation loops with different Burgers vectors: $1/2[111]$ in blue, $1/2[\bar{1}\bar{1}1]$ or $1/2[1\bar{1}1]$ in red, $[010]$ in yellow, respectively. It seems to be that irradiation at 400 °C produced a primarily $1/2\langle 111 \rangle$ type and fewer $\langle 100 \rangle$ type dislocation loops in Figure 8, which is consistent with the results of Z. Yao et al. [23]. However, whether the dislocation loop is of the edged type or mixed type needs to be further confirmed. These dislocation loops together are one of the sources for irradiation hardening.

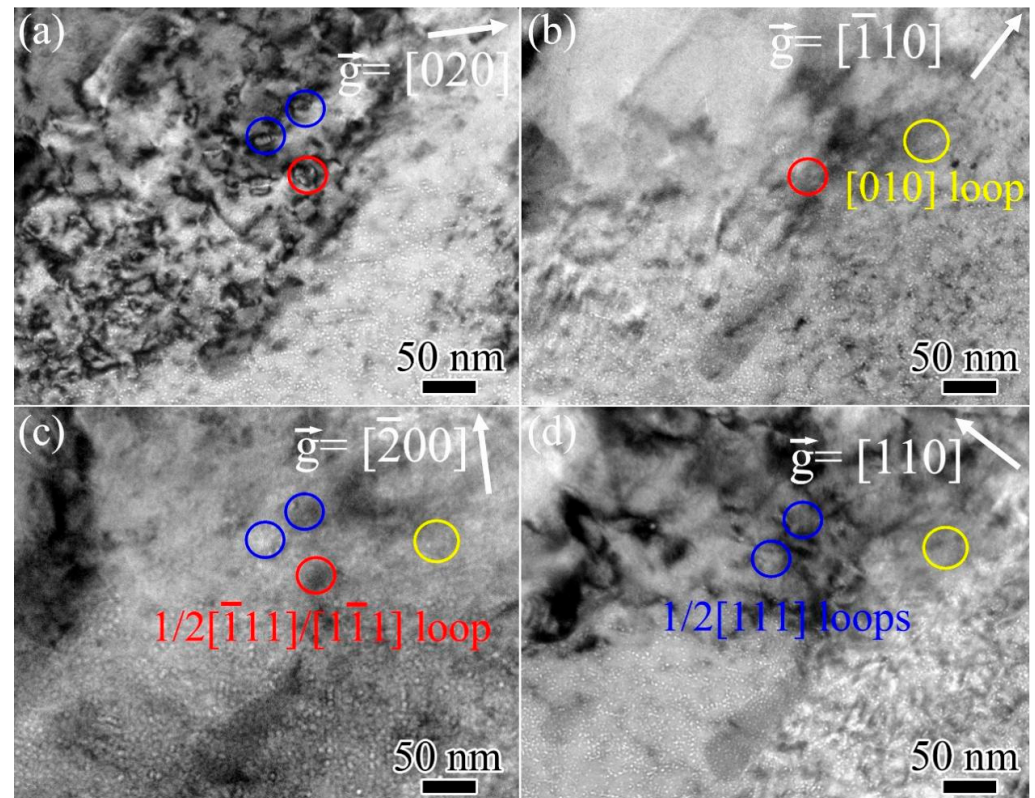


Figure 8. Bright-field images of dislocation loop structures in the matrix of 0.4Si steel under the same zone axis of $z = [001]$ but different g vector conditions: (a) $\vec{g} = [020]$, (b) $\vec{g} = [\bar{1}10]$, (c) $[\bar{2}00]$, and (d) $\vec{g} = [110]$. The sample was irradiated at 400 °C with a fluence of 2×10^{16} ions/cm². Dislocation loops with $[010]$ and $1/2\langle 111 \rangle$ Burgers vectors are highlighted using yellow, blue, and red colors, respectively.

Table 4. Type criterion for dislocation loops near the [001] zone axis.

g·b	1/2[111]	1/2[1̄11]	1/2[11̄1]	1/2[1̄1̄1]	[100]	[010]	[001]
200	V	V	V	V	V	I	I
110	V	I	I	V	V	V	I
020	V	V	V	V	I	V	I
1̄10	I	V	V	I	V	V	I

I: Invisible. V: Visible.

According to the dispersed barrier hardening (DBH) model, the contribution of dislocation loops to irradiation hardening is formulated as [41]:

$$\Delta\sigma_{loop} = \alpha M \mu b \sqrt{d \cdot N}, \quad (5)$$

where $\alpha = 0.45$ is the barrier strength, d and N are the average size and number density of dislocation loops. To evaluate the effect of dislocation loops on irradiation hardening, the number densities of 0Si and 0.4Si steels irradiated at 400 °C were counted and are listed in Table 2. For the same composition, high-fluence (1×10^{17} ions/cm²) irradiation resulted in higher loop size and number density compared to low-fluence (2×10^{16} ions/cm²). Si addition promoted an increase in the number density of loops, which is consistent with other reported results, and the mechanism may be as follows: the atomic radius of Si (1.1 Å) is smaller than that of Fe (1.26 Å) and thus can be solidly solved into the matrix. In addition, it is still an under-sized atom compared to other alloying elements (Cr, W, V, Ta) and can strongly bind with self-interstitial atoms, thus hindering the migration of self-interstitial atoms, and as a consequence, the dislocation loops are difficult to absorb self-interstitial atoms to grow, leading to an increase in the number density of dislocation loops [10]. By Equation (5), the yield strength induced by dislocation loops can be calculated as 0.093 GPa and 0.163 GPa under lower fluence and 0.175 GPa and 0.203 GPa under higher fluence for 0Si and 0.4Si steels, respectively. The corresponding ΔH_{loop} is determined as 0.28, 0.49, 0.52 and 0.61 GPa, respectively, which is much larger than that induced by He bubbles, implying that dislocation loops are the main driver of He²⁺ irradiation-induced hardening in the F/M steel. Therefore, the simple summed calculated irradiation hardening values for low- and high-fluence of 0Si and 0.4Si are 0.35, 0.56, 0.59, and 0.71 GPa, respectively, which are almost consistent with the experimental results.

In addition, the contributions of helium bubbles and dislocation loops to irradiation hardening have a superposition relationship [10]:

$$\Delta\sigma_{total} = \sqrt{\Delta\sigma_{bubble}^2 + \Delta\sigma_{loop}^2}, \quad (6)$$

Combining Equations (3) and (5), the irradiation hardening value (ΔH) estimated by the root sum square method can be expressed as:

$$\Delta H = 3M\mu b \sqrt{\alpha_{bubble}^2 d_{bubble} N_{bubble} + \alpha_{loop}^2 d_{loop} N_{loop}}, \quad (7)$$

where α_{bubble} and α_{loop} are the barrier strength factor of helium bubbles and dislocation loops, d_{bubble} and d_{loop} , and N_{bubble} and N_{loop} are the mean diameter and number density of helium bubbles and dislocation loops, respectively. Fitting the hardness values measured by the nanoindentation with Equation (7) gives the fitted barrier strength factor (α_{bubble} and α_{loop} , Table 5) [10]; however, it seems that α_{loop} matches the results of the previous study (0.2–0.5), while α_{bubble} is lower than the results of the previous study [42]. Then ΔH estimated by the root sum square method can be obtained, as shown in Table 5. The irradiation hardening values calculated by this method are similar to those calculated by the simple summation method, although closer to those fitted with the Nix-Gao model, implying that the root sum square method may be able to estimate the irradiation hardening value more accurately than the simple summation method, probably because the former

takes into account the actual existing superposition of helium bubbles and dislocation loops. The deviations may be caused by, on the one hand, the measurement errors in the size and number density of dislocation loops and helium bubbles due to complex diffraction contrast differences, and on the other hand, the difference in the zones of hardness tests and TEM observations [40].

Table 5. Fitted barrier strength factor of bubbles and dislocation loops, and irradiation hardening obtained by Nix-Gao model, FKH + DBH models (simple summation) and DBH model (root sum square). The unit of ΔH : GPa.

	Conditions	ΔH (Nix-Gao Model)	ΔH (FKH + DBH Models, Simple Summation)	α_{bubble}	α_{loop}	ΔH (DBH Model, Root Sum Square)
0Si	2×10^{16} ions/cm ²	0.3	0.35	0.13	0.39	0.47
	1×10^{17} ions/cm ²	0.9	0.56	0.13	0.39	0.64
0.4Si	2×10^{16} ions/cm ²	0.8	0.59	0.16	0.32	0.65
	1×10^{17} ions/cm ²	1.1	0.71	0.16	0.32	0.77

4. Conclusions

The effects of Si addition on microstructure and mechanical properties in F/M were investigated by He²⁺ irradiation with two fluences at different temperatures, and the main conclusions are as follows:

(1) High-density He bubbles formed in the matrix of F/M steels caused by He²⁺ irradiation, and, as effective defect-adsorption traps, the lath boundary and phase boundary in the F/M steel are noted to be preferential locations for nucleation and growth of He bubbles. In comparison with the case of the Si-free sample, the He bubbles in the 0.4Si sample had a smaller size and higher density at the same fluence owing to the inhibiting effect of Si atoms on He bubble growth.

(2) TEM observation for 0.4Si steel irradiated at 400 °C with a fluence of 2×10^{16} ions/cm² revealed that 1/2<111> and <100> types dislocation loops were induced by He²⁺ irradiation in the F/M steels. Compared to the slight contribution of He bubbles, these dislocation loops were recognized as the main source of irradiation hardening. The addition of Si in the F/M steel promoted an increase in the number density of dislocation loops that exacerbated the irradiation hardening effects.

Author Contributions: Conceptualization, G.Z.; methodology, J.Y.; software, G.Z. and Y.H.; validation, J.Y., Q.F. and X.W. (Xianping Wang); formal analysis, Z.X., L.Z., R.L. and Q.F.; investigation, J.Y., Z.X., R.L., M.S., Y.H. and X.W. (Xuebang Wu); resources, G.L., H.W., X.W. (Xuebang Wu) and C.L.; data curation, G.Z. and X.W. (Xianping Wang); writing—original draft preparation, G.Z.; writing—review and editing, X.W. (Xianping Wang); visualization, X.W. (Xianping Wang); supervision, J.Y. and X.W. (Xianping Wang); project administration, Q.F. and X.W. (Xianping Wang); funding acquisition, Q.F. and X.W. (Xianping Wang). All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by the National Natural Science Foundation of China [Grant Numbers U1967211, 51971212, 51971213, 521011591], the HFIPS Director's fund [Grant Number YZJJ202206-CX], the fund of Science and Technology on Reactor Fuel and Materials Laboratory (Grant No. 6142A06200310), and Anhui Provincial Key R&D Program (Grant No. 202104a05020027). And the APC was funded by [U1967211].

Data Availability Statement: Data is available on reasonable request.

Acknowledgments: The authors want to thank the National Natural Science Foundation of China [Grant Numbers U1967211] and 320 kV high-voltage platform in the Institute of Modern Physics in Lanzhou, China.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Klueh, R.L. Ferritic/martensitic steels for advanced nuclear reactors. *Trans. Indian Inst. Met.* **2009**, *62*, 81–87. [\[CrossRef\]](#)
2. Dvoriashin, A.M.; Porollo, S.I.; Konobeev, Y.V.; Budylnin, N.I.; Mironova, E.G.; Ioltukhovskiy, A.G.; Leontyeva-Smirnova, M.V.; Garner, F.A. Mechanical properties and microstructure of three Russian ferritic/martensitic steels irradiated in BN-350 reactor to 50 dpa at 490 °C. *J. Nucl. Mater.* **2007**, *367–370*, 92–96. [\[CrossRef\]](#)
3. Li, P.; Dai, J.; Wang, L.; Zhou, Y.; Wang, Z.; Xue, K. The effect and mechanism of closed double equal channel angular pressing deformation on He⁺ irradiation damage of low activation steel. *Fusion Eng. Des.* **2023**, *187*, 113358. [\[CrossRef\]](#)
4. Maloy, S.A.; Natesan, K.; Holcomb, D.E.; Fazio, C.; Yvon, P. Overview of Reactor Systems and Operational Environments for Structural Materials in Gen-IV Fission Reactors. In *Structural Alloys for Nuclear Energy Applications*; Elsevier: Amsterdam, The Netherlands, 2019; pp. 23–49.
5. Yao, C.; Zhang, H.; Chang, H.; Shen, T.; Zhu, Y.; Pang, L.; Cui, M.; Wei, K.; Xu, Y.; Wang, D.; et al. Structure of surface oxides on martensitic steel under simultaneous ion irradiation and molten LBE corrosion. *Corros. Sci.* **2022**, *195*, 109953. [\[CrossRef\]](#)
6. Schroer, C.; Koch, V.; Wedemeyer, O.; Skrypnik, A.; Konys, J. Silicon-containing ferritic/martensitic steel after exposure to oxygen-containing flowing lead–bismuth eutectic at 450 and 550 °C. *J. Nucl. Mater.* **2016**, *469*, 162–176. [\[CrossRef\]](#)
7. Hosoi, Y.; Wade, N.; Kunimitsu, S.; Urita, T. Precipitation behavior of laves phase and its effect on toughness of 9Cr-2Mo Ferritic-martensitic steel. *J. Nucl. Mater.* **1986**, *141–143*, 461–467. [\[CrossRef\]](#)
8. Zhang, L.; Yan, W.; Shi, Q.; Li, Y.; Shan, Y.; Yang, K. Silicon enhances high temperature oxidation resistance of SIMP steel at 700 °C. *Corros. Sci.* **2020**, *167*, 108519. [\[CrossRef\]](#)
9. Porollo, S.I.; Dvoriashin, A.M.; Konobeev, Y.V.; Garner, F.A. Microstructure and mechanical properties of ferritic/martensitic steel EP-823 after neutron irradiation to high doses in BOR-60. *J. Nucl. Mater.* **2004**, *329–333*, 314–318. [\[CrossRef\]](#)
10. Chen, Y.; Long, Y.; Luo, H.; Xie, Z.; Lin, W.; Guo, L.; Wang, H.; An, X.; Kong, Q.; Zhang, W.; et al. Effects of different silicon content on irradiation defects and hardening in 9Cr ferritic/martensitic steel. *J. Nucl. Mater.* **2022**, *571*, 154026. [\[CrossRef\]](#)
11. Dudko, V.; Belyakov, A.; Molodov, D.; Kaibyshev, R. Microstructure Evolution and Pinning of Boundaries by Precipitates in a 9 pct Cr Heat Resistant Steel During Creep. *Metall. Mater. Trans. A* **2011**, *44*, 162–172. [\[CrossRef\]](#)
12. Cabet, C.; Dalle, F.; Gaganidze, E.; Henry, J.; Tanigawa, H. Ferritic-martensitic steels for fission and fusion applications. *J. Nucl. Mater.* **2019**, *523*, 510–537. [\[CrossRef\]](#)
13. Fedorova, I.; Belyakov, A.; Kozlov, P.; Skorobogatykh, V.; Shenkova, I.; Kaibyshev, R. Laves-phase precipitates in a low-carbon 9% Cr martensitic steel during aging and creep at 923 K. *Mater. Sci. Eng. A* **2014**, *615*, 153–163. [\[CrossRef\]](#)
14. Zdorovets, M.V.; Kozlovskiy, A.L.; Borgekov, D.B.; Shlimas, D.I. Influence of irradiation with heavy Kr¹⁵⁺ ions on the structural, optical and strength properties of BeO ceramic. *J. Mater. Sci. Mater. Electron.* **2021**, *32*, 15375–15385. [\[CrossRef\]](#)
15. Kozlovskiy, A.L.; Zdorovets, M.V. Effect of doping of Ce^{4+/3+} on optical, strength and shielding properties of (0.5-x)TeO₂-0.25MoO-0.25Bi₂O₃-xCeO₂ glasses. *Mater. Chem. Phys.* **2021**, *263*, 124444. [\[CrossRef\]](#)
16. Henaish, A.M.; Darwish, M.A.; Hemeda, O.M.; Weinstein, I.A.; Soliman, T.S.; Trukhanov, A.V.; Trukhanov, S.V.; Zhou, D.; Dorgham, A.M. Structure and optoelectronic properties of ferroelectric PVA-PZT nanocomposites. *Opt. Mater.* **2023**, *138*, 113402. [\[CrossRef\]](#)
17. Zhao, D.; Li, S.; Wang, X.; Wang, Y.; Liu, F.; Cao, X. Proton irradiation induced defects in T92 steels: An investigation by TEM and positron annihilation spectroscopy. *Nucl. Instrum. Methods Phys. Res. Sect. B Beam Interact. Mater. At.* **2019**, *442*, 59–66. [\[CrossRef\]](#)
18. Zushi, M.; Hashimoto, N.; Hamaguchi, D.; Watanabe, Y.; Tanigawa, H. Helium effect on the sink strength of grain boundaries in F82H. *Nucl. Mater. Energy* **2020**, *25*, 100788.
19. Dauben, P.; Wahi, R.P.; Wollenberger, H. Bubble nucleation and growth in an Fe-12 at% Cr ferritic alloy under He⁺ implantation and Fe⁺ irradiation. *J. Nucl. Mater.* **1986**, *141–143*, 723–726. [\[CrossRef\]](#)
20. Davis, T.P.; Auger, M.A.; Hofer, C.; Bagot, P.A.J.; Moody, M.P.; Armstrong, D.E.J. Nanocluster evolution and mechanical properties of ion irradiated T91 ferritic-martensitic steel. *J. Nucl. Mater.* **2021**, *548*, 152842. [\[CrossRef\]](#)
21. Fukumoto, K.I.; Mabuchi, T.; Yabuuchi, K.; Fujii, K. Irradiation hardening of stainless steel model alloy after Fe-ion irradiation and post-irradiation annealing treatment. *J. Nucl. Mater.* **2021**, *557*, 153296. [\[CrossRef\]](#)
22. Huang, X.; Shen, Y.; Li, Q.; Li, X.; Zhan, Z.; Li, G.; Li, Z. Effect of irradiation temperature on the nanoindentation behavior of P92 steel with thermomechanical treatment. *Nucl. Eng. Technol.* **2022**, *54*, 2408–2417. [\[CrossRef\]](#)
23. Yao, Z.; Jenkins, M.L.; Hernández-Mayoral, M.; Kirk, M.A. The temperature dependence of heavy-ion damage in iron: A microstructural transition at elevated temperatures. *Philos. Mag.* **2010**, *90*, 4623–4634. [\[CrossRef\]](#)
24. Lu, Y.; Zhang, Y.H.; Ma, E.; Han, W.Z. Relative mobility of screw versus edge dislocations controls the ductile-to-brittle transition in metals. *Proc. Natl. Acad. Sci. USA* **2021**, *118*, e2110596118. [\[CrossRef\]](#) [\[PubMed\]](#)
25. Lu, Y.; Shu, X.; Liao, X. Size effect for achieving high mechanical performance body-centered cubic metals and alloys. *Sci. China Mater.* **2018**, *61*, 1495–1516. [\[CrossRef\]](#)
26. Huang, R.; Li, Q.-J.; Wang, Z.-J.; Huang, L.; Li, J.; Ma, E.; Shan, Z.-W. Flow Stress in Submicron BCC Iron Single Crystals: Sample-size-dependent Strain-rate Sensitivity and Rate-dependent Size Strengthening. *Mater. Res. Lett.* **2015**, *3*, 121–127. [\[CrossRef\]](#)
27. Daghbouj, N.; Sen, H.S.; Čížek, J.; Lorinčík, J.; Karlík, M.; Callisti, M.; Čech, J.; Havránek, V.; Li, B.; Krsjak, V.; et al. Characterizing heavy ions-irradiated Zr/Nb: Structure and mechanical properties. *Mater. Des.* **2022**, *219*, 110732. [\[CrossRef\]](#)

28. Daghbouj, N.; Sen, H.S.; Callisti, M.; Vronka, M.; Karlik, M.; Duchoň, J.; Čech, J.; Havránek, V.; Polcar, T. Revealing nanoscale strain mechanisms in ion-irradiated multilayers. *Acta Mater.* **2022**, *229*, 117807. [\[CrossRef\]](#)
29. Chen, Y.; Li, Y.; Ran, G.; Li, G.; Liu, X.; He, K.; Han, Q.; Wang, H.; Huang, X. In-situ TEM observation of microstructure evolution in Fe₉Cr_{1.5}W_{0.4}Si alloy during He⁺ irradiation and post-implantation annealing. *J. Nucl. Mater.* **2021**, *555*, 153126. [\[CrossRef\]](#)
30. Darwish, M.A.; Zubar, T.I.; Kanafyev, O.D.; Zhou, D.; Trukhanova, E.L.; Trukhanov, S.V.; Trukhanov, A.V.; Henaish, A.M. Combined effect of microstructure, surface energy, and adhesion force on the friction of PVA/ferrite spinel nanocomposites. *Nanomaterials* **2022**, *12*, 1998. [\[CrossRef\]](#)
31. Kozlovskiy, A.; Egizbek, K.; Zdorovets, M.V.; Ibragimova, M.; Shumskaya, A.; Rogachev, A.A.; Ignatovich, Z.V.; Kadyrzhanov, K. Evaluation of the efficiency of detection and capture of manganese in aqueous solutions of FeCeO_x nanocomposites doped with Nb₂O₅. *Sensors* **2020**, *20*, 4851. [\[CrossRef\]](#)
32. Agayev, F.G.; Trukhanov, S.V.; Trukhanov, A.V.; Jabarov, S.H.; Ayyubova, G.S.; Mirzayev, M.N.; Trukhanova, E.L.; Vinnik, D.A.; Kozlovskiy, A.L.; Zdorovets, M.V.; et al. Study of structural features and thermal properties of barium hexaferrite upon indium doping. *J. Therm. Anal. Calor.* **2022**, *147*, 14107–14114. [\[CrossRef\]](#)
33. Gao, Q.; Yuan, Z.; Ma, Q.; Yu, L.; Li, H. Strengthening and toughening optimizations of novel G115 martensitic steel: Utilizing secondary normalizing process. *Mater. Sci. Eng. A* **2022**, *852*, 143621. [\[CrossRef\]](#)
34. Gao, R.; Cheng, B.; Zeng, L.F.; Miao, S.; Hou, J.; Zhang, T.; Wang, X.P.; Fang, Q.F.; Liu, C.S. Microstructure, hardness and defect structure of the He irradiated ODS ferritic steel. *J. Alloys Compd.* **2017**, *691*, 653–658. [\[CrossRef\]](#)
35. Song, P.; Morrall, D.; Zhang, Z.; Yabuuchi, K.; Kimura, A. Radiation response of ODS ferritic steels with different oxide particles under ion-irradiation at 550 °C. *J. Nucl. Mater.* **2018**, *502*, 76–85. [\[CrossRef\]](#)
36. Yang, Y.; Zhang, C.; Meng, Y.; Liu, J.; Gou, J.; Xian, Y.; Song, Y. Nanoindentation on V–4Ti alloy irradiated by H and He ions. *J. Nucl. Mater.* **2015**, *459*, 1–4. [\[CrossRef\]](#)
37. Chen, C.L.; Richter, A.; Kögler, R.; Talut, G. Dual beam irradiation of nanostructured FeCrAl oxide dispersion strengthened steel. *J. Nucl. Mater.* **2011**, *412*, 350–358. [\[CrossRef\]](#)
38. Nix, W.D.; Gao, H. Indentation size effects in crystalline materials: A law for strain gradient plasticity. *J. Mech. Phys. Solids* **1998**, *46*, 411–425. [\[CrossRef\]](#)
39. Zhang, G.J.; Zhou, Y.; Yang, J.F.; Yang, H.Y.; Wang, M.M.; Jing, K.; Xie, Z.M.; Zhang, L.C.; Liu, R.; Li, G.; et al. Effect of Si content on the microstructure and mechanical properties of 9Cr-ferritic/martensitic steels. *Nucl. Mater. Energy* **2023**, *35*, 101428. [\[CrossRef\]](#)
40. Wei, Y.P.; Liu, P.P.; Zhu, Y.M.; Wang, Z.Q.; Wan, F.R.; Zhan, Q. Evaluation of irradiation hardening and microstructure evolution under the synergistic interaction of He and subsequent Fe ions irradiation in CLAM steel. *J. Alloys Compd.* **2016**, *676*, 481–488. [\[CrossRef\]](#)
41. Gupta, G.; Was, G.S. Improved Creep Behavior of Ferritic-Martensitic Alloy T91 by Subgrain Boundary Density Enhancement. *Metall. Mater. Trans. A* **2007**, *39*, 150–164. [\[CrossRef\]](#)
42. Bergner, F.; Pareige, C.; Hernández-Mayoral, M.; Malerba, L.; Heintze, C. Application of a three-feature dispersed-barrier hardening model to neutron-irradiated Fe–Cr model alloys. *J. Nucl. Mater.* **2014**, *448*, 96–102. [\[CrossRef\]](#)

Disclaimer/Publisher's Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.