Microstructure and Nano-Hardness of 10 MeV Cl-Ion Irradiated T91 Steel*

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Abstract Hardening and elemental segregation of T91 martenstic steel irradiated by 10 MeV Cl ions to doses from 0.06 dpa to 0.83 dpa were investigated with the nanoindentation technique and transmission electron microscopy (TEM). The results demonstrated that the irradiation hardening was closely related with irradiation dose. By increasing the dose, the hardness increased rapidly at first from the initial value of 3.15 GPa before irradiation, and then tended to saturate at a value of 3.58 GPa at the highest dose of 0.83 dpa. Combined with TEM observation, the mechanism of hardening was preliminary attributed to the formation of $M(Fe,Cr)_{23}C_6$ carbides induced by the high energy Cl-ion irradiation.

Keywords: ferritic/martensitic steel, irradiation damage, nano-hardness

(Some figures may appear in colour only in the online journal)

1 Introduction

Ferritic/martensitic (FM) steels have been regarded as the primary candidate structural materials of fusion reactors, advanced fission reactors, sub-critical accelerator driven systems (ADS) as well as other advanced nuclear systems [1−3]. Different from traditional industrial materials, nuclear materials are used under a severe radiation environment, and various irradiation induced damages, such as irradiation swelling and hardening, will lead to great degradation of mechanical and thermal performances. Among all of the FM steels, T91 ferritic/martensitic steel had attracted wide interest because of its favorable properties, including low corrosion, good swelling resistance, high thermal conductivity and good fatigue strength at high temperature [4,5]. As structural materials in nuclear systems, irradiation resistance of FM steels is a very key parameter because the extremely stringent conditions in nuclear systems unavoidably make structural materials suffer serious irradiation damages. To precisely predict such degradation and elucidate the mechanisms, it is of great importance to investigate systematically the microstructural evolution of nuclear materials under various irradiation conditions.

A high energy ion irradiation experiment had been widely used as an effective tool to simulate neutron irradiation damage in structural materials [6], because it can also cause similar damages to that in the neutron irradiation environment, including defect clusters and dislocation loops, radiation-induced segregation, and cracks, etc. More importantly, high energy ion irradiation can effectively avoid activating materials, reduce irradiation time as well as control the irradiation conditions precisely, including irradiation dose, irradiation flux and irradiation temperature, etc. However, one typical demerit of ion irradiation is the inhomogeneity of irradiation damage owing to the micrometer-scale penetration depth of the ion beam; as a result the damage region is limited only to the nearby surface on the irradiated sample. Because of the small damage region in ion irradiation, it is difficult to measure and evaluate the variation of mechanical properties by conventional methods. The nanoindentation technique has proved to be a useful technique to characterize the irradiation effects in structural materials owing to its highly-accurate depth-sensing loading method [7,8]. Based on a nanoindentation measurement, the slight hardness change induced by ion irradiation can be effectively acquired on a nanometer scale.

In the previous research of ion irradiation damage in FM structural materials, the applied irradiation ions were dominantly Proton, self-ion Fe and inert gas elements (He, Ar, Xe) due to limited experimental conditions, while other heavy ions, especially halogen elements, are seldom used. It is thus not clear whether halogen element irradiation will induce similar irradiation damage behaviors, such as irradiation hardening

Table 1. The chemical compositions of T91 steel (wt.%)

Element	Cr	Ni	Mo	Mn	V	Nb	C	Si	P	N	Fe
Content	8.32	0.09	0.86	0.48	0.2	0.06	0.092	0.15	0.012	0.055	Bal.

and irradiation-induced segregation, etc. In this paper, the microstructural evolution and irradiation hardening of T91 steel irradiated by a high energy Cl-ion beam were investigated by nanoindentation technique combined with microstructure analysis. The preliminary experimental results demonstrated that typical irradiation damage behaviors could also be caused by high energy Cl ions as induced by other heavy ions.

2 Experimental details

The T91 steel samples used in this investigation were cut from an industrial ingot and the corresponding chemical compositions are listed in Table 1. Prior to ion irradiation, the specimens were polished sequentially by 600-2000 grit emery papers at first, and then annealed at 923 K for 5 h in a vacuumed furnace with a low pressure of 10^{-3} Pa to remove the possible internal stress in the samples.

The irradiation experiments were carried out in the Institute of Heavy Ion Physics at Peking University, and the chosen radiation resource was high energy Cl^{3+} ions. The detailed irradiation parameters were described as follows: A 2×6 MeV tandem accelerator was used to implant 10 MeV chlorine ions with an ion flux of 100 nA and fluence of 2.4×10^{14}-7.0×10^{15} ions/cm^2 at room temperature, resulting in a total displacement dose of about 0.06-0.83 dpa. Depth profiles of the displacement damage for a 10 MeV Cl-ion beam with fluence of 7.0×10^{15} ions/cm^2 were calculated by the SRIM code [9], as shown in Fig. 1. The displacement damage peak D_{dam} and the maximum penetration depth H_{max} were calculated as about 2.1 μm and 2.5 μm, respectively.
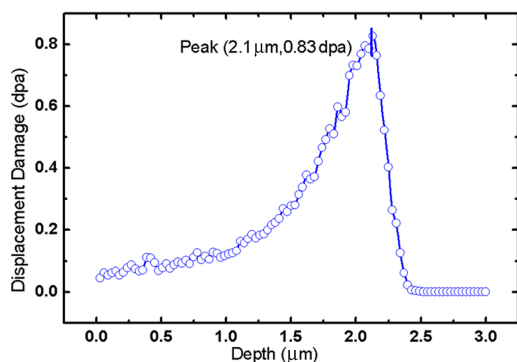

Fig.1 Displacement damage (dpa) versus depth for T91 steel irradiated with 10 MeV Cl^{3+} ion beam as calculated by SRIM

The microstructure analysis of the irradiated T91 steel samples was characterized by high resolution transmission electron microscopy (HRTEM, JEM-2010FX) equipped with a selected area electron diffraction system (SAED) and an energy dispersive X-ray analytical system (EDX, INCA). The nanoindentation measurement of the T91 steel samples was carried out by an Agilent Nano Indenter G200 with a Berkovich three-sided diamond pyramid and an optical microscope. The Berkovich diamond indenter tip was shaped as a centerline-to-face angle of 65.3° and 20 nm in radius, and a continuous stiffness measurement (CSM) was used to continuously obtain the hardness (H)-depth (h) profile with a single indent up to a depth of about 2 μm, which ensured that the maximum indentation depth was limited in the irradiated area. The resolution of the displacement and load in the nanoindentation measurement were adjusted to be about 0.02 nm and 50 nN, respectively.

3 Results and discussion

Fig. 2 demonstrates the indentation depth dependence of the load for the un-irradiated and high energy Cl-ion irradiated T91 steel samples. As for the irradiated samples, only one specimen with an irradiation dose of 0.44 dpa is shown as an example. It is revealed that the load of the irradiated sample is higher than that of the un-irradiated one for the same indentation depth, indicating the appearance of induced irradiation hardening.
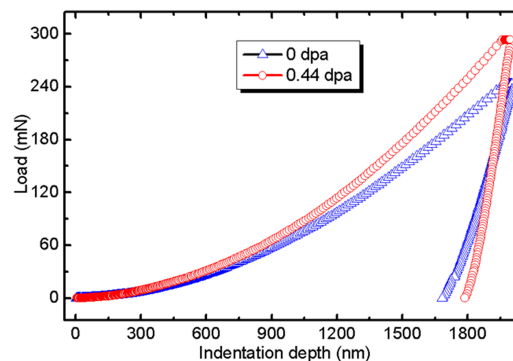

Fig.2 Load versus indentation depth of the unirradiated and the irradiated T91 steel samples

To obtain the value of nano-hardness more precisely, 6-8 indents are measured for each sample, and Fig. 3 shows the representative indentation-depth profiles of a sample irradiated with a dose of 0.44 dpa. By carefully comparing the profiles of each indent, no significant difference is observed if the indentation depth is larger than 100 nm. However in the indentation depth range less than 100 nm, the hardness values are relatively scattered owing to the effect of surface roughness and limitation of the CSM methodology [10,11]. In the indentation depth range larger than 100 nm, the hardness value decreases smoothly with the increasing indentation depth, which is the so-called "indentation size effect" (ISE) [12].
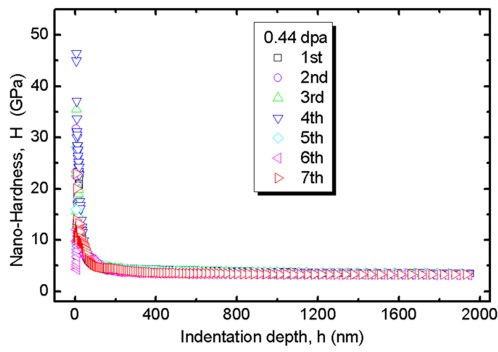
Fig.3 Indentation depth dependence of the nano-hardness for the irradiated T91 sample with ion dose 0.44 dpa

Fig. 4 shows the indentation depth profiles of the nano-hardness for the unirradiated and the irradiated T91 steel samples. The irradiation dose varies from 0.03 dpa to 0.83 dpa. According to the SRIM simulation, the effective damage region induced by Cl-ion irradiation was mainly located in a depth ranging between 1.0 μm and 2.1 μm. Therefore, we are concerned with the variation of hardness in the indentation depth between 1000 nm and 2000 nm in this investigation. As can be seen from Fig. 4, the nano-hardness is found to gradually increase with an increase in the irradiation dose, as shown more clearly in the local enlarged inset.
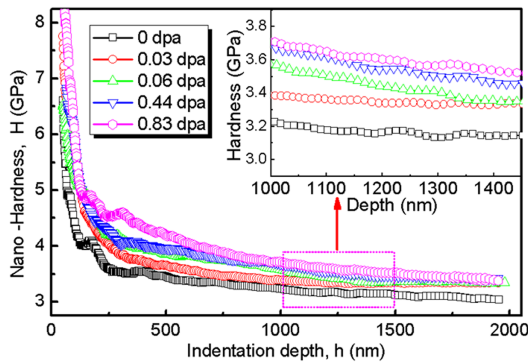

Fig.4 Indentation-depth profiles of the nano-hardness for T91 steel samples under different Cl^{3+} irradiation doses

The average nano-hardness of the un-irradiated and the irradiated T91 steel samples obtained from an indentation depth of 1000 nm to 2000 nm are plotted in Fig. 5 as a function of irradiation dose. It can be seen that with an increase in irradiation dose, the hardness increases rapidly from the initial value of 3.16 GPa to 3.47 GPa at 0.06 dpa, and then gradually saturates at a values of 3.58 GPa at the highest dose of 0.83 dpa. The result obviously indicates that the irradiation induced hardening effects in T91 steel already occurred seriously at the beginning of the irradiation.

It is well known that one of the typical characteristics of ion irradiation for F/M steel is irradiation induced hardening. Zhu et al. studied the irradiation hardening of T91 steel by high energy self-ion Fe with an irradiation dose of 3 dpa at room temperature, and found that the nano-hardness increased from about 3.5 GPa before irradiation to 3.8 GPa after irradiation [13]. After being irradiated by 27.4 MeV He ions, Jung et al. found that the hardness of T91 steel enhanced from 2.9 GPa for

the unirradiated sample to 3.2 GPa after irradiation at a dose of 0.8 dpa [14]. Using proton irradiation, Gupta et al. observed the irradiation hardening phenomenon in which the hardness of the T91 sample increased by about 13.3% after being irradiated by a 2.0 MeV proton with a dose of 3 dpa [15]. It is worth noting that in our investigation, a typical irradiation hardening effect also occurs in the T91 steel sample after irradiation by high energy Cl ions, which implies that halogen-ion irradiation can induce similar damage to that caused by proton and other heavy ion irradiation.
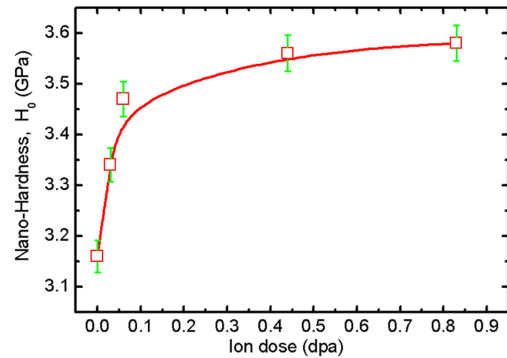

Fig.5 Average hardness versus Cl^{3+} irradiation dose, deduced between indentation depths of 1000 nm and 1500 nm

In order to understand the mechanism of hardening induced by high energy Cl ion irradiation, TEM observation was carried out to investigate the evolution of the microstructure of T91 steel samples. Fig. 6 gives a typical comparison of a microstructure for the un-irradiated and the irradiated samples. In the un-irradiated sample (Fig. 6(a)), dark particles, as labeled by white arrows, are observed to disperse in both grain boundaries and grain interiors. After irradiation, however, typical irradiation-induced precipitation was found, as shown in Fig. 6(b), where the TEM result at 0.06 dpa is presented as an example. It is noted that after irradiation, precipitates increase in number and in size. Moreover, the precipitates induced by Cl-ion irradiation tended to segregate to grain boundaries, which is quite different from the random dispersion in the un-irradiated samples.
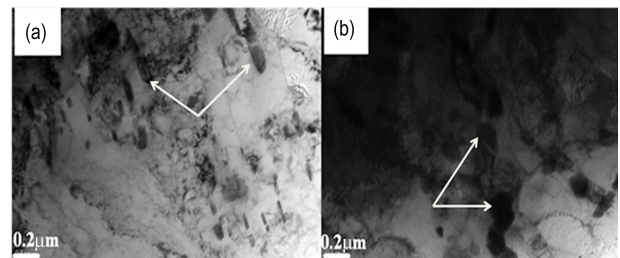

Fig.6 TEM images of T91 steel samples under different Cl^{3+} irradiation doses: (a) as-supplied, (b) 0.06 dpa

The TEM-EDS analysis, as shown in Fig. 7, reveals that the compositions of the precipitates (labeled in Fig. 6 by white arrows) are dominantly Fe, Cr, and C elements. A high intensity of C line in the EDS spectrum evidences that such precipitates are actually carbides. The selected-area electron diffraction (SAED),

as shown in Fig. 8, reveals that the dominant phase of the precipitates embedded in the T91 steel matrix can be regarded as $M(Fe,Cr)_{23}C_6$ carbides, which is similar to the results reported in Ref. [16]. The appearance of high density and large size carbide precipitates is possibly associated with the segregation of the C element induced by high energy Cl^{3+} ion irradiation. Normally, carbide precipitates need to grow up at a relatively high temperature; the observed growth of segregation carbide in this investigation was possibly caused by the increase of local temperature at the T91 steel surface induced by high-energy ion irradiation.
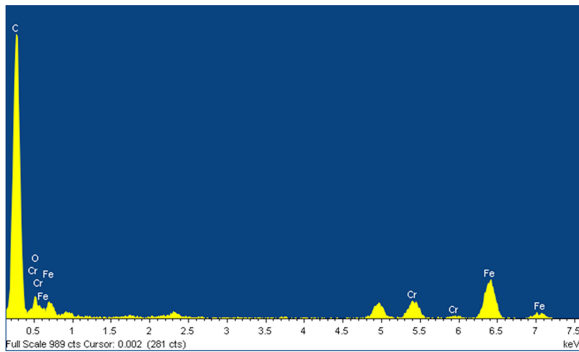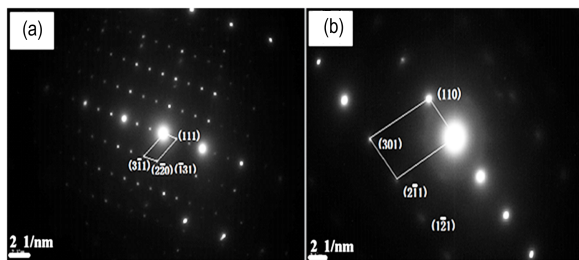

Fig.7 TEM-EDS spectrum of the carbides

Fig.8 SAED patterns: (a) α-Fe matrix, (b) carbides

It is well known that the irradiation hardening is generally caused by the formation of voids, precipitates, and/or dislocation loops that impede the motion of dislocations. Our experimental results evidence that the formation of irradiation induced $M(Fe,Cr)_{23}C_6$ carbides can be recognized as the main reason for the hardening. During the nano-hardness measurement, such carbides can act as obstacles to the free movement of dislocations, and thus increase the indentation hardness of the T91 steel. Similar irradiation induced segregation and hardening were also observed in the microstructural evolution of proton irradiated T91 steel [15]. It is worth pointing out that in FM steels the elemental segregation would significantly affect the mechanical properties. In particular, the segregation of Cr and C elements would result in the formation of brittle phase $Cr_{23}C_6$, and thus degrade the mechanical properties such as fracture toughness.

4 Conclusion

In the present investigation, the nanoindentation test and TEM observation were applied to evaluate the irradiation induced hardening and elemental segregation in T91 martensitic steel irradiated with 10 MeV high energy Cl ions. The experimental results provide clear evidence that halogen-ion irradiation can induce similar damage to that in proton and other heavy ion irradiation. The main results can be summarized as follows:

a. Irradiation induced hardening was observed in all the irradiated T91 steel samples. The nano-hardness increases rapidly at the beginning stage of irradiation, and then tends to saturate at the damage level of 0.83 dpa.

b. TEM analysis clearly indicated the formation of irradiation induced segregation, and SAED further revealed that the dominant phase of the precipitates embedded in the T91 matrix was $M(Fe,Cr)_{23}C_6$ carbides.

c. Based on nanoindentation results and TEM observations, the mechanism of hardening is suggested to originate mainly from the formation of $M(Fe,Cr)_{23}C_6$ carbides induced by high energy Cl-ion irradiation.

Acknowledgment

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