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Effect of hydrogen ion/electron dual-beam irradiation on microstructural damage of a 12Cr-ODS ferrite steel

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A B S T R A C T

The effect of hydrogen ion/electron dual-beam irradiation on the microstructural evolution of a new 12Cr-ODS ferrite steel made by chemical soaking method (CSM) was investigated. The results showed that the dislocations were introduced at the initial stage of irradiation and then developed into dislocation networks. The void swellings after the irradiation to a dose of 15 dpa were less than 0.15%. The interface between the dispersed oxide particle and the matrix became irregular due to the irradiation; while the macroscopic size change of the oxide particle was not recognized, thus suggesting that the steel had a good resistance to irradiation during the dual-beam irradiations between 623 K and 823 K. The formation of voids with small mean size and high number density was closely concerned with hydrogen which would assist the void nucleation as a result of hydrogen ion trapping vacancies during the irradiation.

1. Introduction

It has been reported that oxide dispersion strengthened (ODS) materials have a great applicability because of their excellent mechanical properties and swelling resistance under irradiation at medium and high temperatures. Within the framework of nuclear applications, ODS-based Fe alloys are considered as potential candidates for some structure components subjected to high neutron environment at high temperature (400–700 °C) [1]. Additionally transmutation effects of H and He are important issues for spallation materials.

The ODS steel, usually produced by mechanical alloying, has high temperature creep strength because of the existence of fine grains (3–10 μm) and dispersed nanometer oxide particles in ferrite matrix. During the rolling process of ODS steel, problems such as anisotropic structure, recrystallization at a high temperature and retained ferrite can not be thoroughly solved. In order to resolve these problems, chemical soaking method is used to produce ODS steel with addition of Y_2O_3 particles. In the steel produced by CSM, size distributions of grains and Y_2O_3 particles are 40–50 μm, and 10–200 nm, respectively. The steel has high strength and excellent plasticity [2].

When the steel made by CSM would be applied to the use for nuclear power reactors, especially in the environments where the irradiation induced defects are introduced and simultaneously hydrogen is introduced due to the existence of nuclear transmutation in the steel, the effect of oxide particle on damage structures should be investigated, because chemical and mechanical properties of steel would be influenced by the damage structures.

In the present work, as a simulation experiment, by considering not only irradiation induced defects but also transmutated hydrogen effect, newly prepared ODS steel was characterized assuming the conditions of nuclear reactors in hydrogen environment.

2. Experimental procedures

Chemical composition of the steel was Fe–12.5Cr–2.5W–0.25Ti–0.4Y_2O_3 (mass%). The master alloy was melted in vacuum induction furnace and forged into bars with 25 mm diameters. The pre-alloyed powder in size of 50–150 μm was made by nitrogen atomization after the bars being annealed at 1523 K for 1.5 h. The powder was soaked in $Y(NO_3)_3 \cdot H_2O$ solution, followed by drying and heating in a hydrogen gas atmosphere in order to deposit the Y_2O_3 particles on the surface of the pre-alloyed powder. After hot isostatic pressing and forged into bars, the material was solution annealed at 1223 K for 2 h and then air cooled. The specimens were solution treated at 1323 K for 0.5 h in vacuum and quenched by water, then thinned to ⩽0.15 mm and punched into 3 mm discs. The discs were electro-polished for the transmission electron microscopy observation.

The dual-beam irradiation was carried out by implanting 50 ppm/dpa hydrogen ion by the ion accelerator with the voltage of about 33 keV. By using HVEM at 1250 kV with a damage rate of approximately 2×10^{-3} dpa/s, the electron irradiation was

Abbreviations: CSM, chemical soaking method; ODS, oxide dispersion strengthened; HVEM, high voltage electron microscope.

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carried out to a maximum dose of 15 dpa, thus the total amount of hydrogen was 750 ppm. The irradiation temperatures were 623 K, 723 K and 823 K, respectively. The thickness of the irradiation foil was 500 nm and the foil crystalline planes were (1 1 0) or (1 1 1).

3. Results

3.1. Microstructure at the initial stage of irradiation

Before the irradiation, low number density dislocations which were pinned by oxide particles existed in the matrix. As shown in Fig. 1, during the dual-beam irradiation at 623 K, dark dots (cluster of interstitials) were observed on/around the dislocations. When the irradiation dose increased to 3.4 dpa, the number of the dots increased and a part of the dots grew into dislocation loops. Simultaneously, the small voids could be observed near the dislocation loops. As the irradiation dose increased to 6.8 dpa, with the amount of hydrogen of 340 ppm, the dislocation loops disappeared due to climbing, while the small voids still remained at the same sites. The same void distributions were observed at 723 K and 823 K.

3.2. Formation of the voids

The distributions of voids and dislocation loops after irradiation at various temperatures and doses are shown in Fig. 2. The images of the voids were not so clear because of a large number of dislocation loops and strain contrast caused by the loops. The photos were taken on condition of under focus to avoid the interference of the dislocation loops.

Between 623 K and 823 K, the voids were observed around the oxide particles and in the matrix, but the oxide part looked like more preferential nucleation site. In Fig. 3, the mean size (a) and the number density (b) of voids were shown as a function of the dose.

At 623 K, the voids grew larger and the number density remained high as the dose increased. The void mean size was 6.48 nm with the dose of 15 dpa.

As the irradiation temperature increased to 723 K, with the dose of 10 dpa, the mean size and the number density of voids were 4.34 nm and $1.29 \times 10^{22}\ m^{-3}$, respectively. The fine voids remained high number density at the higher doses.

The void number density was lower at the temperature of 823 K than that of 723 K. With the increase of dose, the mean size of voids became larger, while the number density remained high.

3.3. Stability of the oxide particles under irradiation

The ODS steel containing Y_2O_3 oxide particles with various sizes was dual-beam irradiated. During the irradiation, the oxide particles of 5–10 nm showed no obviously change before and after the irradiation of 15 dpa, which meant that the oxides were stable under irradiation, as shown in Fig. 4. However, the interface

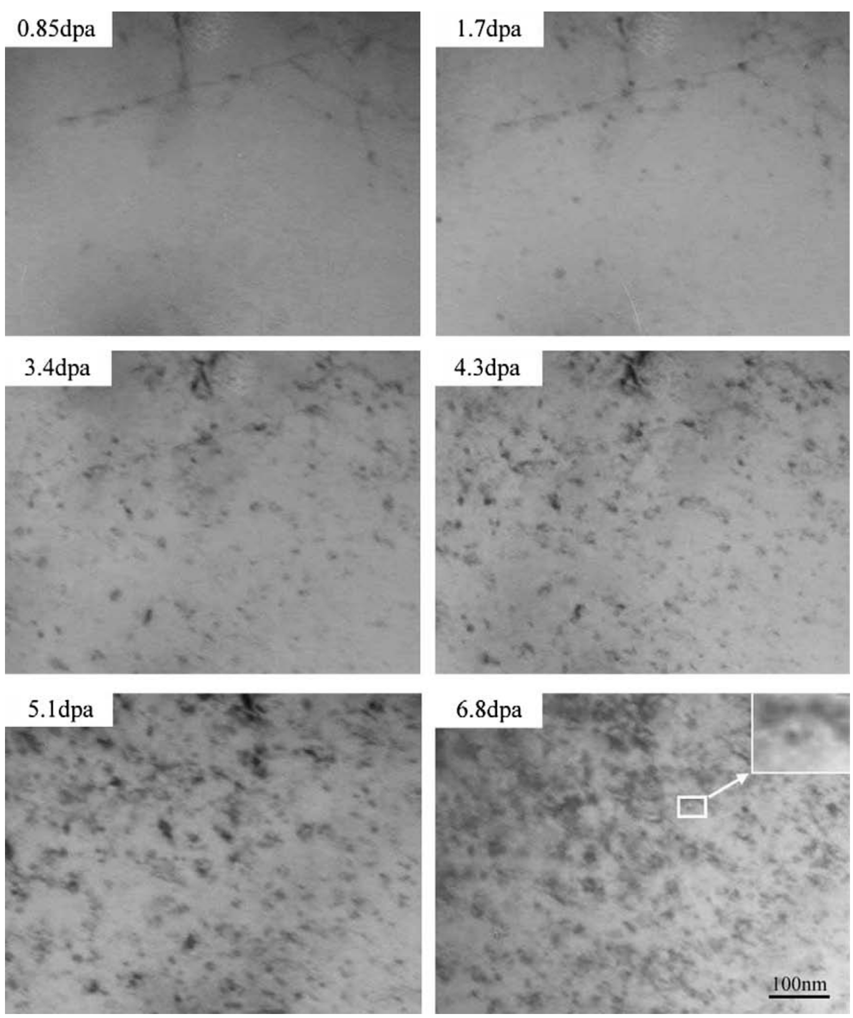

Fig. 1. Microstructures at the initial stage of irradiation at 623 K of the 12Cr-ODS steel.

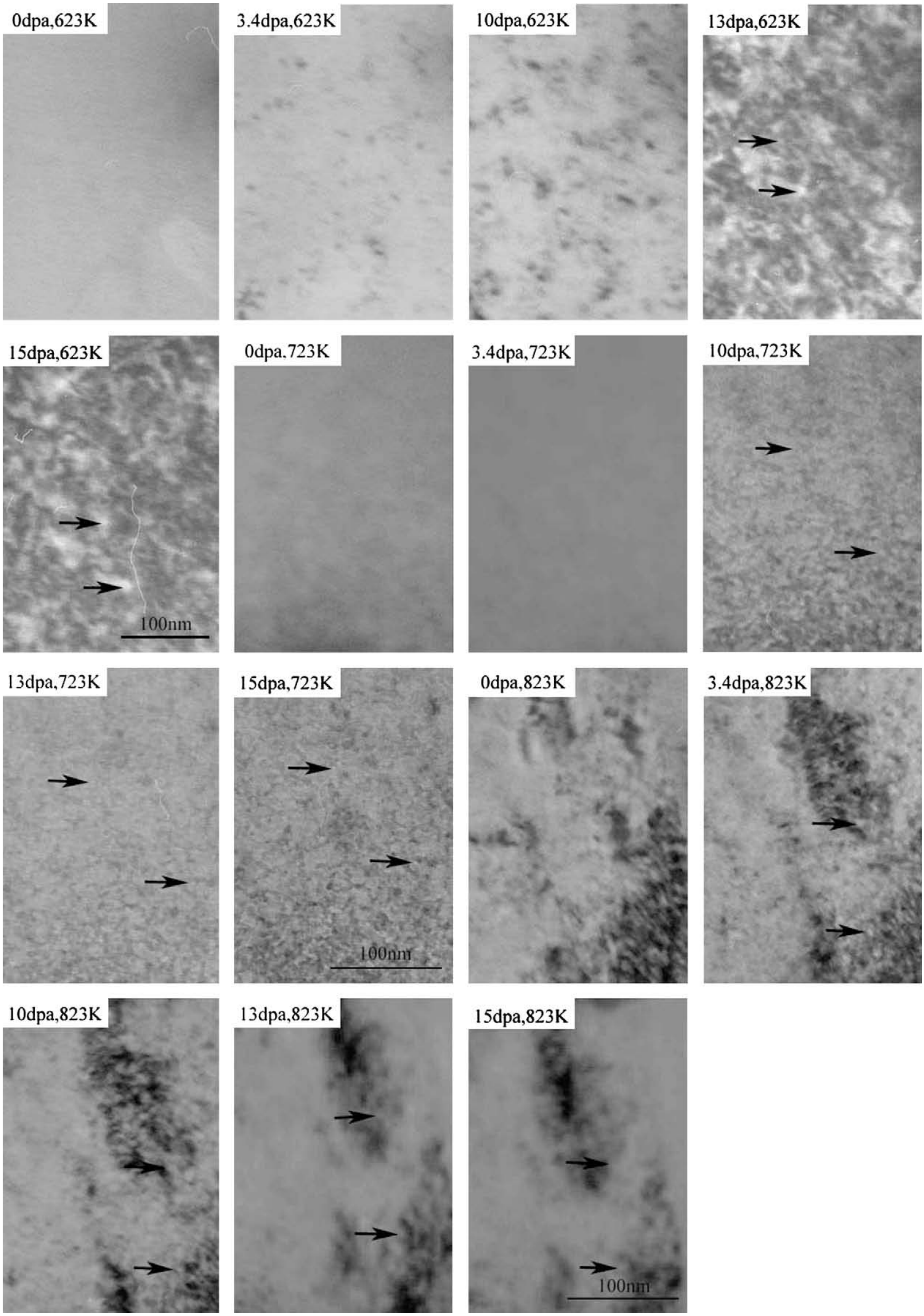

Fig. 2. Void formation in the 12Cr-ODS steel at various temperatures and doses.

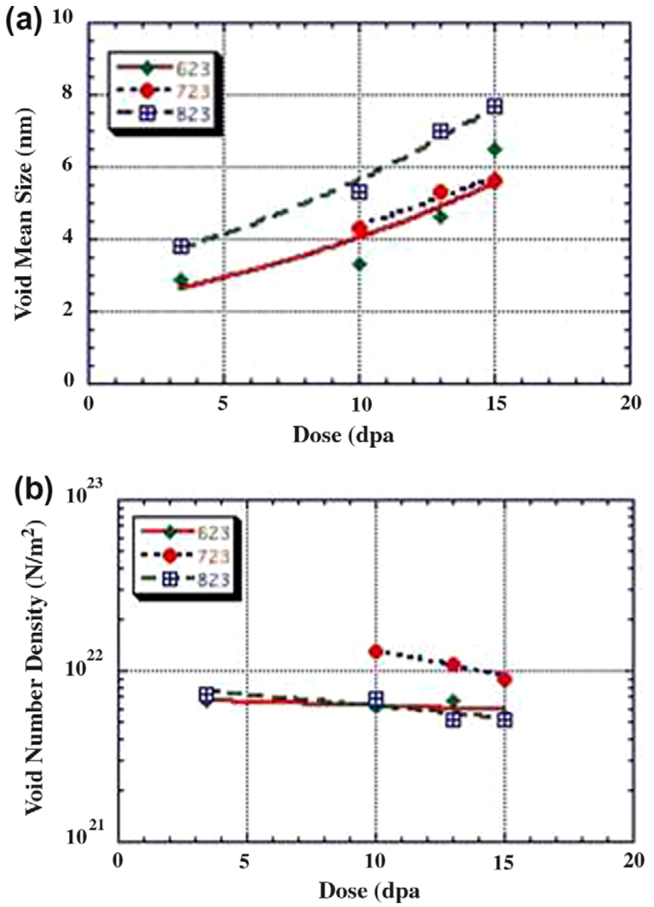

Fig. 3. Relationship between mean size and dose (a), number density and dose (b).

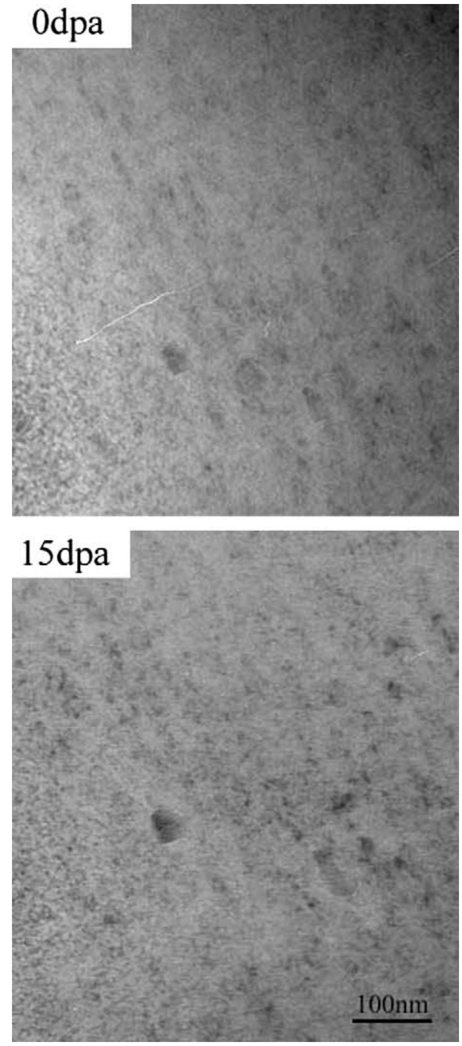

Fig. 4. Morphologies of oxides before and after irradiation at 723 K.

between large Y_2O_3 particle and the matrix became irregular after the larger oxide was irradiated at 723 K. This irregular interface might attribute to the defects flowed into the interface.

Thus even the interface structure microscopically changed, but on these irradiation conditions, the macroscopic size change of the oxide particles was not recognized, as shown in Fig. 5.

4. Discussion

4.1. Microstructural damage at the initial stage of dual-beam irradiation

A plenty of dark dots were observed at the initial stage of irradiation, as shown in Fig. 1. The dots number increased greatly with the increase of dose, while the growth rate of the dots was low. The dots finally disappeared as being evolved into the dislocation loops, which were recognized as the interstitial dislocation loops. A number of interstitial atoms and vacancies (Frankel pairs) were introduced under the irradiation and the former defects migrated more easily than the latter. Interstitial atoms gathered during transferring to the sink to reduce the system energy, and then the atoms turned into interstitial dislocation loops. Accordingly, the number density of vacancies in the matrix increased, and the vacancies turned into H–V complex because of the strong interaction between the vacancies and hydrogen ions [3]. When the H–V complex grew to the critical size, the number of the complex would decrease because the complex greatly absorbed the interstitial atoms. During this process, a part of interstitial atoms were consumed and the growth rate of the interstitial dislocation loops was slowed down since the interstitial atoms concentration decreased. It can be concluded that the implanted hydrogen ion enhances the formation of the dislocation loops but inhibits their growth.

4.2. Formation and swelling of voids

The experimental results showed that the fine voids with high number density formed under the dual-beam irradiation. The void size increased slightly with the increase of dose and temperature. For example, when temperature and dose increased from 623 K to 823 K, and 3.4 dpa to 15 dpa, respectively, the mean size of voids increased from about 3 nm to 8 nm, as shown in Fig. 3a, while the void number density tended to decrease slightly from $7.25 \times 10^{21}\ m^{-3}$ to $5.24 \times 10^{21}\ m^{-3}$ when the dose increased from 3.4 dpa to 15 dpa at 823 K (see Fig. 3b). The formation of small voids with high number density was observed remarkably as a characteristic behavior under the irradiation with hydrogen ion implanted.

The effect of implanted hydrogen ion on the void formation should be closely related to the diffusion of hydrogen behaviors in steel. Hydrogen ion diffuses fast in iron steel with a coefficient of $10^{-8}\ m^2/s$ even at room temperature. Moreover, hydrogen ions interact with vacancies, and form vacancy clusters with hydrogen. The binding energy of hydrogen ion and vacancy is 0.2–0.6 eV [4,5]; this strong interaction between hydrogen ion and vacancy

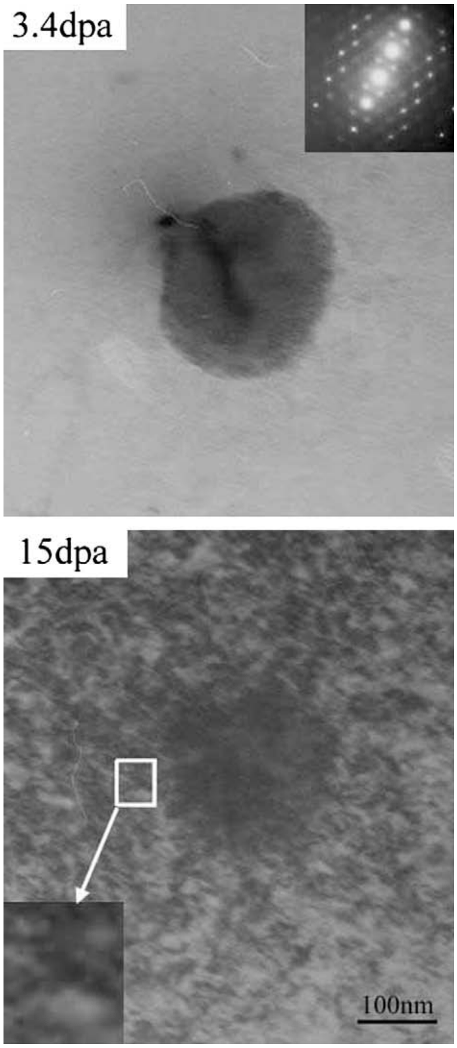

Fig. 5. Morphologies of oxides before and after irradiation at 623 K.

contributes to the void nucleation during the formation of H–V complex.

The void number density could be 10^{21}–10^{23} m^{-3} in hydrogen ion implanted alloys, and the dislocations in the hydrogen ion implanted ODS steel could be in a high density of 10^{11}–10^{12} m^{-2}. These facts indicate that the implanted hydrogen ions influence the stable nucleation of voids and dislocation loops. Moreover, when hydrogen atoms exist as hydrogen gas in the voids, the internal pressure of the voids would increase, which make the voids more stable.

The void swellings of the ODS steel were low under hydrogen ion implanted condition; with the increase of irradiation temperature and dose, the swellings increased slowly. As shown in Fig. 6, after the irradiation with a dose of 15 dpa, the void swellings of all irradiated specimens were less than 0.15%, which indicated that the 12Cr-ODS steel had a good resistance to irradiation.

4.3. Stability of dispersed Y_2O_3 particles

As the generation IV super critical water-cooled reactor cladding material, the stability of the oxide particles is very important for the evaluation of irradiation damage on ODS ferrite steel. In past years, plenty of works on this field have been published. An experimental irradiation in Phénix of a ODS ferrite type alloy, named DY, indicated that Y_2O_3 dissolved under neutron irradiation

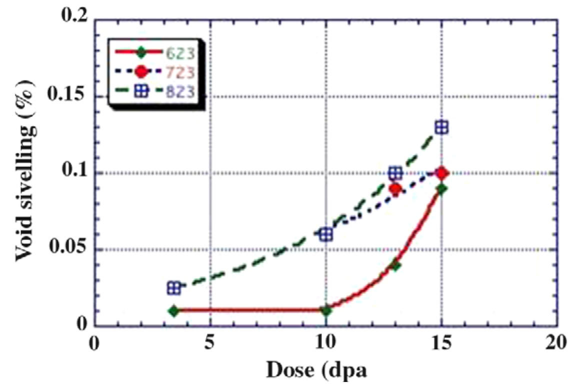

Fig. 6. Relationship between void swelling and irradiation dose.

with the dose of 80 dpa [6]. Monnet et al. [7] also reported that electron irradiation led to a significant dissolution of oxides with a radius decrease proportional to the dose. The displacement energies of Y and O in Y_2O_3 are 57 eV, and that of iron is 40 eV. The atom displacement damage is easy to be induced by the irradiation in ferrite steel, which results in high number density voids in steel. The diffusion of voids from ferrite to Y_2O_3 particle along the density gradient would cause the dissolution of oxide.

However, it has also been reported that dispersed Y_2O_3 particles are stable under a heavy irradiation. Yoshitake et al. [8,9] observed that the oxide particles were stable under neutron irradiation with the dose of 15dpa in the experimental fast reactor of JOYO; the strength and the toughness of the material did not change. Allen et al. [10] reported that the structures of unirradiated and irradiated 9Cr-ODS steel were the same under the Ni ion irradiation at 723 K with different doses of 5, 10 and 15 dpa, which meant that the Ti–Y complex oxides were stable under the irradiation.

In the present work, the oxide particles in various sizes were stable with the dose up to 15 dpa. It should be pointed out that the dispersed oxides were obtained by chemical soaking method, by which the stoichiometric ratio of Y and O was stable. Since $\Delta_f G^{\theta}_{Y_2O_3}$ is lower than $\Delta_f G^{\theta}_{Y_2TiO_5}$ and $\Delta_f G^{\theta}_{Y_2Ti_2O_7}$, Y_2O_3 is in the better thermal stability than Y_2TiO_5 and $Y_2Ti_2O_7$. The number density and the diffusion coefficient of second defect increased with hydrogen ion implanted; and the interface between the oxide and the matrix became irregular since the free defects diffused into the oxide. As Gan et al. [11] pointed out, the oxide particles and the microstructure of 9Cr-ODS showed minimal change under certain condition, and the dislocation had no multiplication, which was in agree with the present work.

5. Conclusions

In the present study, 12Cr-ODS ferrite steel made by chemical soaking method was firstly irradiated under hydrogen ion/electron dual-beam; and the conclusions are as follows:

1. The implanted hydrogen ion had a significant effect on the microstructural damage at the initial stage of irradiation. The dislocation loops were in small size, had high number density, and low growth rate. Hydrogen enhanced the nucleation but inhibited the growth of the dislocation loops.
2. Hydrogen could greatly improve the effective nucleation sites of voids, but inhibit their growth. The voids were also in small size, had high number density, low growth rate and small swelling.
3. Part of the interfaces between the oxide particles and the matrix became irregular under the irradiation. The oxide particles were stable with no dissolution.

4. The formation of voids with small size and high number density should be concerned closely with fast diffusion rate, low migration activation energy and strong capacity of trapping vacancies of hydrogen ion during irradiation.

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