Formation of Vacancy-Type Dislocation Loops in Hydrogen-Ion-Implanted Fe–Cr Alloy

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Abstract

Fe–10 at.%Cr alloy was implanted with hydrogen ions at room temperature, followed by annealing at high temperatures. The annealing process made the defects develop into large dislocation loops. The nature of the dislocation loops formed after annealing was studied by the evolution of loops under in situ electron irradiation in high-voltage electron microscope. It indicated that only interstitial-type loops were observed when annealed at 550 °C and below, but vacancy-type loops started to form at the temperature higher than 600 °C. According to the previous study of our group, the presence of chromium element made the formation temperature of vacancy-type loops higher than that in pure iron. The effect of alloying elements on the formation temperature of the vacancy-type loops was discussed.

Keywords Hydrogen implantation · Interstitial-type loops · Vacancy-type loops · Fe–Cr alloy · High-voltage electron microscope

1 Introduction

Reduced activation ferritic/martensitic (RAFM) steels, based on Fe–Cr alloys, have been considered as one of the most promising candidate structural materials for future fusion reactors [1–3]. During service, these steels will be irradiated by intense fluxes of highly energetic particles such as neutrons, α particles and protons [4]; thus, they exhibit irradiation swelling, low-temperature hardening, etc., after irradiation [5]. Dislocation loops as one of the most common microstructures of irradiation in materials contribute largely to this material degradation in synergy with small bubbles, voids and interstitial clusters and so on [6].

The nature of dislocation loops, e.g., interstitial type or vacancy type, as well as their Burgers vectors, is the key factor for the microstructure evolution of irradiation damage. The bias effect of dislocation loops on point defects

would influence irradiation swelling of materials [7]. Gao et al. [8] experimentally demonstrated that the bias factor of interstitial-type loops was higher than that of vacancy-type loops. In addition, a computer simulation also predicted that interstitial loops would contribute a larger effect on radiation hardening than vacancy loops [9].

Dislocation loops in iron-based materials have been widely reported in the related papers [10–12]. Eyre and Bartlett firstly investigated dislocation loops in neutron-irradiated α -Fe and observed $1/2 \langle 111 \rangle$ loops by the electron microscope [13]. Almost at the same time, Master found $\langle 100 \rangle$ loops in iron foils irradiated with 150 keV Fe^+ ions [14]. Later, both $1/2 \langle 111 \rangle$ loops and $\langle 100 \rangle$ loops were observed in self-ion-irradiated pure iron at 40 K by Robertson, Kirk et al. [15]. Recently, Yao et al. profoundly studied the irradiation temperature (T_{irr}) dependence of heavy-ion damage in iron and reported that at $T_{\text{irr}} \leq 400$ °C, the microstructure was dominated by $1/2 \langle 111 \rangle$ loops of interstitial nature; at 500 °C, only $\langle 100 \rangle$ loops were identified [16]. Now a general consensus on the nature of dislocation loops in iron and ferritic steels has been achieved. The existence of $1/2 \langle 111 \rangle$ and $\langle 100 \rangle$ loops has been confirmed by computer simulations [17, 18] and experimental observations [19, 20]. Effects of alloying elements or impurities on the formation and migration of dislocation loops were also extensively studied

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[19, 21, 22]. However, in most studies, mainly the interstitial-type loops were identified and concerned, and few studies were focused on the vacancy-type loops in iron and ferritic alloys [23, 24].

The previous works of our group have found that after annealing at elevated temperatures, the vacancy-type loops with the size as large as 100 nm could be formed in pure iron implanted by the hydrogen ions or deuterium ions [25–27]. Moreover, adding nickel element in iron could decrease the formation temperature of the vacancy-type loops. It means the nature of dislocation loops is significantly influenced by the alloying elements. However, the effects of alloying elements on the type of dislocation loops are still not clarified in detail.

In the present work, hydrogen ions were preimplanted into a Fe–Cr model alloy at room temperature. The nature of dislocation loops formed during annealing at different temperatures was investigated by in situ observation in high-voltage electron microscope (HVEM). The dependence of the formation temperature of the vacancy-type loops on alloying elements in iron binary alloys was discussed.

2 Materials and Methods

The material used in this study was Fe–10 at.%Cr, a model alloy of RAFM steels. The chemical composition of the specimen is listed in Table 1. Specimens were mechanically milled on both sides to a thickness of 100 μm and then punched into disks of 3 mm in diameter. To eliminate the defects generated during mechanical milling, the specimens were annealed at 700 $^{\circ}\text{C}$ in vacuum for 60 min followed by furnace cooling. The final samples for transmission electron microscopy (TEM) were prepared by twin-jet electro-polishing in Tenupol-5 at -20°C using an electrolyte of 5% HClO_4 + 95% ethanol (volume) solution.

Hydrogen ions with the energy of 30 keV were implanted to the TEM samples at room temperature by an ion accelerator to a dose of 1×10^{17} ions/ cm^2 . Irradiation damage and hydrogen concentration distribution in the alloy are shown in Fig. 1. It was calculated by the software of SRIM-2008 with displacement threshold energy 40 eV in Fe–Cr alloy and based on the Kinchin-Pease calculation

Fig. 1 Displacement damage and hydrogen concentration profile in Fe–10 at.%Cr model alloy after 30 keV hydrogen ion irradiation calculated by SRIM-2008

model [28]. In the observation region (120–160 nm), the average irradiation damage is about 0.45 dpa and the corresponding hydrogen concentration reaches up to 5 at.%.

After hydrogen implantation, the specimens were annealed at 550 $^{\circ}\text{C}$, 600 $^{\circ}\text{C}$, and 620 $^{\circ}\text{C}$, respectively, for 30 min in high vacuum, followed by in situ observation under electron irradiation at the corresponding annealing temperature in JEM1300 high-voltage electron microscope (HVEM) in Hokkaido University, Japan. The accelerating voltage of JEM1300 HVEM is 1250 kV. The damage rate induced by electrons is 0.002 dpa/s.

As is known, the inside–outside method is usually applied to identify the nature of dislocation loops [29]. It is reliable for dislocation loops with a size of larger than 5 nm by showing the contrast change of two-type dislocation loops in bright-field images under $\pm g$ vectors. Here in our study, in situ electron irradiation was used to determine the nature of dislocation loops, which was pioneered by Kiritani et al. [30]. The defects produced by electron irradiation are pure Frankel pairs, i.e., vacancy–interstitial pairs. The higher mobility of interstitials than vacancies results in more interstitial atoms interacting with a dislocation loop during electron irradiation. Consequently, the interstitial-type dislocation loops are expected to grow, while the vacancy-type ones should shrink or disappear during the electron irradiation. This difference of mobility between interstitials and vacancies can be used to identify the type of a dislocation loop.

3 Results

After hydrogen implantation at room temperature, a large number of tiny defects formed in the specimen of Fe–10 at.%Cr alloy as shown in Fig. 2. It was reported that

Table 1 The chemical composition of Fe–Cr alloy

Specimen	Cr (wt%)	C (wt%)	N (wt%)
Fe–Cr alloy	9.43	0.013	0.008

Fig. 2 TEM images of Fe-10at.%Cr **a** before, **b** after hydrogen implantation

these small defects were supposed to be dislocation loops of interstitial-type because of the low irradiation temperature [31]. However, these tiny dislocation loops are too small to identify their nature. The density and size of these tiny loops depend on the irradiation conditions and the post-annealing temperature and time. When annealed at higher temperature, these tiny loops will migrate and coalesce to form large dislocation loops, with a lower density. Further elevating the annealing temperature, vacancy clusters also become mobile and start to migrate that can result in the annihilation of interstitial clusters and the formation of vacancy-type loops.

The annealing experiments of the specimens were carried out inside the column of HVEM without electron irradiation by a heating holder, allowing hydrogen-implantation-induced defect clusters to develop into larger dislocation loops. After aging at 550 °C for 30 min, the specimen was subjected to the electron irradiation in HVEM at the same temperature. The in situ observation of the loops evolution is shown in Fig. 3. During the electron irradiation, all of the loops are observed to grow. Among them, two adjacent dislocation loops coalesce with each other and finally become one loop. The size of the grown dislocation loops was measured as a function of the irradiation time. According to the slope of the fit line as shown in Fig. 4, the growth rate of the tracked loops has been obtained. To get more reliable results, for each irradiation temperature, 3–5 loops have been measured. In Fig. 4, the fit line (a) represents that the average growth rate of loops at 550 °C is about 2.2 nm/min.

As mentioned above, electron irradiation produces an interstitial dominant atmosphere during the early stage of irradiation because of higher mobility of interstitials than vacancies. As a result, interstitial-type dislocation loops are expected to grow and the corresponding vacancy-type

loops to shrink or even disappear. Therefore, according to the result, it could be known that the dislocation loops formed at 550 °C in Fe-10 at.%Cr alloy preimplanted with hydrogen ions at room temperature are of interstitial type.

Shrinking processes of dislocation loops under the electron irradiation were observed in hydrogen-ion-implanted Fe-10 at.%Cr alloy when annealed at 600 °C as shown in Fig. 5. The dislocation loop in the left bottom corner with the size about 50 nm is getting smaller and smaller with the increase in electron irradiation time. But the shrinking rate of the dislocation loop is 1.89 nm/min at 600 °C as shown in Fig. 4b. It is lower than the growing rate of dislocation loops at 550 °C, though the migration rate of interstitials is faster at 600 °C. This result sufficiently illustrates that the bias of vacancy-type dislocation loops is much weaker than that of interstitial-type dislocation loops in Fe-Cr alloy. Gao et al. directly compared the bias factor of the two types of loops in pure iron under in situ electron irradiation. It suggested that the bias of interstitial-type loops was higher than that of vacancy-type loops, which agrees well with the present experimental result [8]. The observed shrinking dislocation loop is of vacancy type. It can be concluded that vacancy-type dislocation loops are formed at 600 °C in hydrogen-ion-implanted Fe-10 at.%Cr alloy.

When the aging temperature was lifted to as high as 620 °C, the shrinking processes of dislocation loops under the electron irradiation can be still observed in the hydrogen-ion preimplanted Fe-10 at.%Cr alloy as shown in Fig. 6. It suggests that the loops become smaller by absorbing interstitial atoms and at last disappear during electron irradiation. The shrinkage rate of the dislocation loop is as high as 8.56 nm/min, which is higher than that at 600 °C. This phenomenon can be explained reasonably by the higher migration rate of the interstitials at 620 °C than

Fig. 3 Change of loops under electron irradiation at 550 °C in Fe–10 at.%Cr annealed at the same temperature which was preimplanted with hydrogen ions at room temperature

Fig. 4 Size of dislocation loops as a function of electron irradiation time at different temperatures

at 600 °C. As a result, there are still vacancy-type dislocation loops formed at 620 °C in hydrogen-ion-implanted Fe–10 at.%Cr alloy.

4 Discussion

4.1 Formation of Vacancy-Type Dislocation Loops

The vacancy-type loop formation takes place mostly during cascades in copper and other metals [8], but much less readily in pure iron and its corresponding ferritic materials. Gilbert et al. [32] reported that the difficulty for the formation of vacancy-type loops in iron was related to the higher energy configuration of vacancy-type loops than voids. Their simulations also indicated that the stability of loops strongly varied depending on their size. Vacancy-type dislocation loops produced in cascade collapse above a critical diameter (~ 2 nm) were highly metastable due to the difficulty of their transformation into voids. The formation of collapsed vacancy loops has been confirmed experimentally in Fe–11 wt%Cr irradiated with 30 keV Ga⁺ by Yao et al. [33]. Jenkins et al. [34] also showed the formation of $a_0 \langle 100 \rangle$ vacancy loops in pure Fe after irradiation performed with Ni⁺, Ge⁺, Kr⁺, Xe⁺ and W⁺ and energies between 40 keV and 240 keV. In the other hand, JAGER [35] and Yi et al. [36] found vacancy-type dislocation loops formed within individual cascades in tungsten irradiated with 60 keV Au ions and 150 keV self-ions, respectively. But these collapsed vacancy loops formed in the above literatures are very small (< 5 nm) and determined by black–white contrast method. However, in

Fig. 5 Change of loops under electron irradiation at 600 °C in Fe-10 at.%Cr annealed at the same temperature which was preimplanted with hydrogen ions at room temperature

our study, negligible cascade effect is expected due to the lower energy of incident ions. More important is that the vacancy-type loops in the present study are formed during annealing process at high temperature, instead of the ion irradiation process itself. The size of vacancy-type loops is in the range of several tens of nanometers. Therefore, it is reasonable to consider that these loops should form by aggregation of migrating vacancy clusters. An increasing formation of vacancy loops was observed with the increase in annealing temperature, which is consistent with our previous studies [25, 26]. It has been clarified that hydrogen plays an important role in the formation of vacancy-type dislocation loops. Hydrogen atoms are thought to form dumbbells with vacancies leading to the higher structure stability of vacancy-type dislocation loops [25].

4.2 The Effect of Thin Foil Surface

The inevitable drawback of in situ electron irradiation is the surface effect of TEM thin foil specimens. The surfaces affect the irradiation-induced microstructure simply because defects produced in their vicinity can annihilate there if the defects migrate to the free surfaces. Therefore, if an interstitial-type dislocation loop is located near the free surface, it may exhibit shrinkage or disappearance due to its interstitials that migrate to the surface. Horiki et al. [37] have reported this abnormal phenomenon during electron irradiation, e.g., interstitial-type loops shrank or disappeared and vacancy-type loops grew and they were

exclusively located near the surface. However, they as well suggested that no loops behaved abnormally when at the central part of the specimen. Besides, loops lost to the surface during irradiation at high temperature are always in a time range of less than seconds. Therefore, it is rational to believe that the shrinkage or disappearance of the loops observed in our case is due to the absorption of interstitials instead of gliding out of the surface. Recently, by molecular dynamics simulations, Aliaga et al. [38] revealed that vacancy loops tended to form near the free surface of the specimens irradiated with low dose and low-energy ions. They explained that it was resulted from the imbalance in the number of vacancies with respect to self-interstitials, due to the trapping of the latter at the surface. Regarding our case, the TEM film specimen was implanted with low-energy hydrogen ions. When the specimen annealed at temperature as high as 600 °C and above, most interstitials would escape to the surface. The number imbalance between vacancies and interstitials was intensified, which created conditions for the formation of vacancy-type dislocation loops.

4.3 The Effect of Alloying Elements on the Formation Temperature of Vacancy-Type Loops

As mentioned in Sect. 1, our previous study has confirmed that vacancy-type loops formed at 500 °C in pure Fe, but at 450 °C in Fe-1 wt%Ni alloy instead [25]. The presence of

Fig. 6 Change of loops under electron irradiation at 620 °C in Fe–10 at.%Cr annealed at the same temperature which was preimplanted with hydrogen ions at room temperature

alloying element can change the formation temperature of vacancy-type loops. The current experimental results appreciably manifest that vacancy-type loops start to form at 600 °C in hydrogen-ion preimplanted Fe–10 at.%Cr. Different from nickel, adding chromium element in iron could increase the formation temperature of the vacancy-type loops. The essential reason is thought to be related to the effect of the alloying element on the migration of point defects, i.e., interstitials and vacancies. On the one hand, Cr could pin the interstitial-type loops and decrease the mobility of interstitial clusters, which has been confirmed by the experimental results of Yao [33]. Hence, it requires higher temperature to establish the striking number advantage of vacancies with respect to interstitials in Fe–Cr alloy than in pure Fe. On the other hand, Cr atoms, as the bigger size than that of Fe atoms, could bind with vacancies. The trapping effect of vacancies by the solute atoms depends on their size factor. Both Kato [39] and Hackett

[40] pointed out that the bigger the size of the solute atoms, the higher the binding energy with vacancies. Maybe there would be a new method that classifies alloying elements in steels by increasing or decreasing the formation temperature of vacancy-type dislocation loops, compared with the case of pure iron. However, whether or not all of the oversized solute atoms can increase the formation temperature of vacancy-type loops, and meanwhile, all of the undersized solute atoms could decrease it, and this still demands further experiments.

5 Conclusions

The evolution of dislocation loops in the hydrogen-ion-implanted Fe–10 at.%Cr alloy annealed at the temperature from 550 to 620 °C was investigated in situ under electron

irradiation in HVEM. The main results are summarized as follows:

1. At the temperatures below 550 °C, dislocation loops formed in Fe–10 at.%Cr are interstitial type.
2. The vacancy-type dislocation loops in Fe–10 at.%Cr alloy were observed to form at the temperature of 600 °C and above.
3. Comparing with the previous study, the formation temperature of vacancy-type loops would increase by adding chromium to bcc iron.

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