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Observation of c-component dislocation structures formed in pure Zr and Zr-base alloy by self-ion accelerator irradiation

Susumu Yamada [a,*], Takanori Kameyama [b]

[a] Central Research Institute of Electric Power Industry (CRIEPI), Materials Science Research Laboratory, Yokosuka-shi, Kanagawa-ken 240-0196, Japan
[b] Central Research Institute of Electric Power Industry (CRIEPI), Nuclear Technology Research Laboratory, Komae-shi, Tokyo 201-8511, Japan

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ABSTRACT

The microstructures of pure Zr and Zr-base alloy (Zircaloy-2) irradiated with Zr ions (self-ions) were studied by transmission electron microscopy. It was found that the c-component dislocation structures formed in neutron-irradiated Zircaloy-2 can also be obtained by self-ion irradiation. This technique can be used to simulate neutron irradiation and is thus expected to deepen our understanding of irradiation damage in pure Zr and Zr-base alloys.

1. Introduction

The extension of fuel burn-up is a promising way to reduce fuel cycle costs and the amount of spent fuel assemblies in light water reactors (LWRs). Zr-base alloys are widely used as fuel cladding materials in LWRs because of their low neutron absorption rate and high corrosion resistance. However, in recent years it has been reported that the ductility of Zr-base alloys decreases under a high burn-up condition (over 50 MWd/kgU) in LWRs [1,2]. Elucidation of the mechanism of ductility degradation at high burn-up is important from the viewpoint of cladding integrity. Understanding of the mechanism will also be useful in the development of cladding materials tolerant to burn-up extension.

It is well known that irradiation damage in the form of a-component and c-component dislocations is introduced in pure Zr and Zr-base alloys by neutron irradiation [3–7]. The former dislocations are formed on the $(11\bar{2}0)$ prismatic plane and the latter are formed on the (0001) basal plane. It has been reported that the number density of c-component dislocations monotonically increases with increasing fluence; on the other hand, the density of a-component dislocations becomes saturated even at a low fluence and is not clearly dependent on the fluence [8]. Thus, in this study, we focused on c-component dislocations because Ref. [8] indicated that there is a correlation between the growth of c-component dislocations and the degradation of ductility. The c-component dislocation structure has a characteristic well-defined alignment of straight lines parallel to the (0001). However, the effect of irradiation conditions on the formation of the damage structures is not yet clear. One reason for this is that it takes a long time and enormous cost to obtain neutron-irradiated materials irradiated to high fluence. To overcome this problem, ion irradiation with an accelerator is used as a simulation technique to replace neutron irradiation. An advantage of using ion irradiation is that neutron-introduced damage can be simulated in a comparatively short time. However, reports on the simulation of c-component dislocation structures by ion irradiation are still limited. Lee and Koch reported that irradiation damage similar to c-component dislocation structures can be formed in Zircaloy-2 upon 5 MeV Ni ion irradiation [9]. They also showed that the damage structures change with increasing irradiation temperature and fluence, but it is not clear whether the ion-induced dislocations are identical to neutron-induced dislocations, since the Burgers vector of the dislocations has not been clarified [9]. Furthermore, as Ni is ferromagnetic, an unexpected interaction between the injected ions and the matrix (host atoms) may occur. The simplest and effective way to avoid this complication is to use self-ions (Zr ions).

There are hardly any reports on the microstructures of self-ion-irradiated pure Zr and Zr-base alloy. Thus, in the present study, we investigated the effects of the displacement per atom (dpa) value, the irradiation temperature and the presence of alloying elements on the formation of c-component dislocation structures in the materials. We show that the c-component dislocation structures introduced in Zircaloy-2 by neutron irradiation are successfully simulated by the self-ion irradiation in pure Zr and Zircaloy-2.

2. Experimental

The materials subjected to self-ion irradiation were Zircaloy-2 cladding tubes designed for boiling water reactor (BWR) fuel assemblies and polycrystalline Zr sheets of commercial purity.

* Corresponding author.
E-mail address: susumu@criepi.denken.or.jp (S. Yamada).

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Table 1
Chemical compositions of materials used for self-ion irradiation.

Material	Zr	Sn	Fe	Cr	Ni	Hf (%)
Pure Zr[a]	98.56	–	[b]	[b]	–	1.20
Zircaloy-2	98.08	1.52	0.11	0.10	0.05	–

[a] Commercial purity.
[b] Fe + Cr = 0.08.

The chemical compositions of the materials are shown in Table 1. The materials contained also small amounts of H, N and O. Prior to ion irradiation, the surface of the material was electropolished with a solution of 10% perchloric acid and 90% acetic acid after the surface was mechanically polished.

The self-ion irradiation was carried out at the 3 MV tandem accelerator facility of Japan Atomic Energy Agency (JAEA) at Takasaki. The polished surface was exposed to 12 MeV Zr^{4+} ions. The irradiation temperature was maintained at 573 or 673 K, corresponding to actual plant operating temperatures in LWRs, and the damage level was 5, 15, 20 or 40 dpa (Table 2). The damage rate was calculated using the SRIM-2000 simulation code (the stopping and range of ions in matter) [10]. This program can calculate the stopping and range of ions into matter through a quantum mechanical treatment of ion–atom collisions. The damage rate is 7.6×10^{-4} dpa/s in this study, and the irradiation time for which the target dpa value was attained was determined using this damage rate.

As briefly described above, it is known that c-component dislocations form vacancy-type dislocation loops with Burgers vectors of $1/6 < 20\bar{2}3 >$ or $1/2[0001]$ [3–7]. Thus, the vacancy distribution in depths below the surface of pure Zr irradiated with 12 MeV Zr^{4+} ions was calculated by using the SRIM-2000 code. The calculation results show that the region with the greatest damage is at a depth of 2.4 μm. Thin foils (thickness ~100 nm) for transmission electron microscope (TEM) observation were obtained that included the region of the greatest damage and neighboring regions by focused ion beam (FIB) milling (Hitachi FB-2000A). The procedure for specimen preparation is schematically shown in Fig. 1. Two types (cross sections and transverse sections) of specimens were prepared; the cross-section specimens were found more suitable for observing c-component dislocation structures. The thin foils were observed using a field-emission TEM (Hitachi HF-3000) operated at an accelerating voltage of 300 kV.

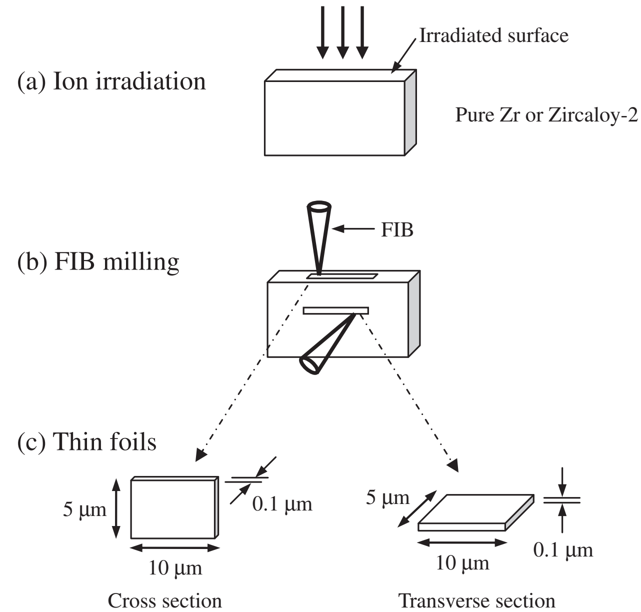

Fig. 1. Schematic diagram showing the procedure for TEM specimen preparation.

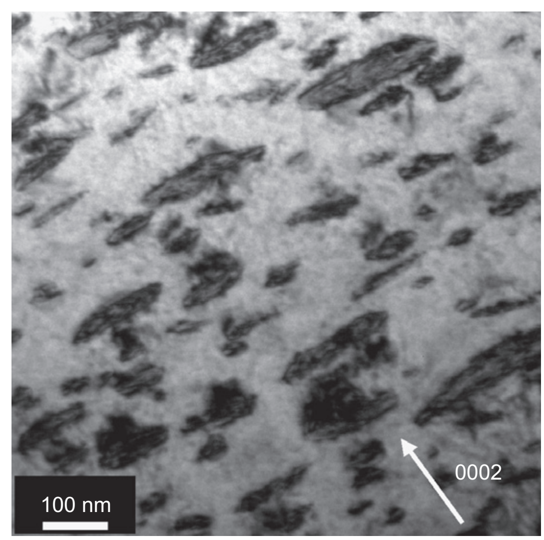

Fig. 2. BF-TEM image of pure Zr before irradiation. White arrow shows diffraction vector.

3. Results

Fig. 2 shows a bright-field (BF) TEM image of pure Zr before irradiation. Zirconium hydrides show dark contrast with a size of 50–200 nm. Hardly any damage due to FIB milling was observed.

Fig. 3 shows a series of BF-TEM images of pure Zr irradiated with self-ions at 673 K to different dpa values. The effect of the damage level on the microstructures is clear. At a low level of 5 dpa, no visible damage occurred and the appearance of the microstructure was similar to that of the preirradiated material (Fig. 2). The image also suggests a decrease in the number density of hydrides, and this decrease should have been caused by elemental diffusion during the irradiation. At higher levels of 15 and 20 dpa, damage structures were clearly formed with an aligned array of linear contrast parallel to the basal plane (0002) with a spacing of about 30–40 nm (Fig. 3b and c). The overall features are very similar to the c-component dislocation structures formed in neutron-irradiated Zircaloy-2 as shown later in Fig. 8.

No clear difference between the damage structures was observed for damage levels of 15 and 20 dpa. Also, at the highest level of 40 dpa, damage structures were clearly formed, as shown in Fig. 3d, but the defect contrast appears to have changed, with the formation of discontinuous segments rather than linear contrast. We consider that this was caused by the excessive accumulation of c-component dislocation loops.

The Burgers vector of the dislocations produced in pure Zr irradiated with self-ions was examined using the invisibility criterion

Table 2
Self-ion irradiation conditions for pure Zr and Zircaloy-2.

Material	Temperature (K)	Damage (dpa)	Irradiation time (s)
Pure Zr	573	20	2.6×10^4
Pure Zr	673	5	0.7×10^4
Pure Zr	673	15	2.0×10^4
Pure Zr	673	20	2.6×10^4
Pure Zr	673	40	5.3×10^4
Zircaloy-2	573	20	2.6×10^4

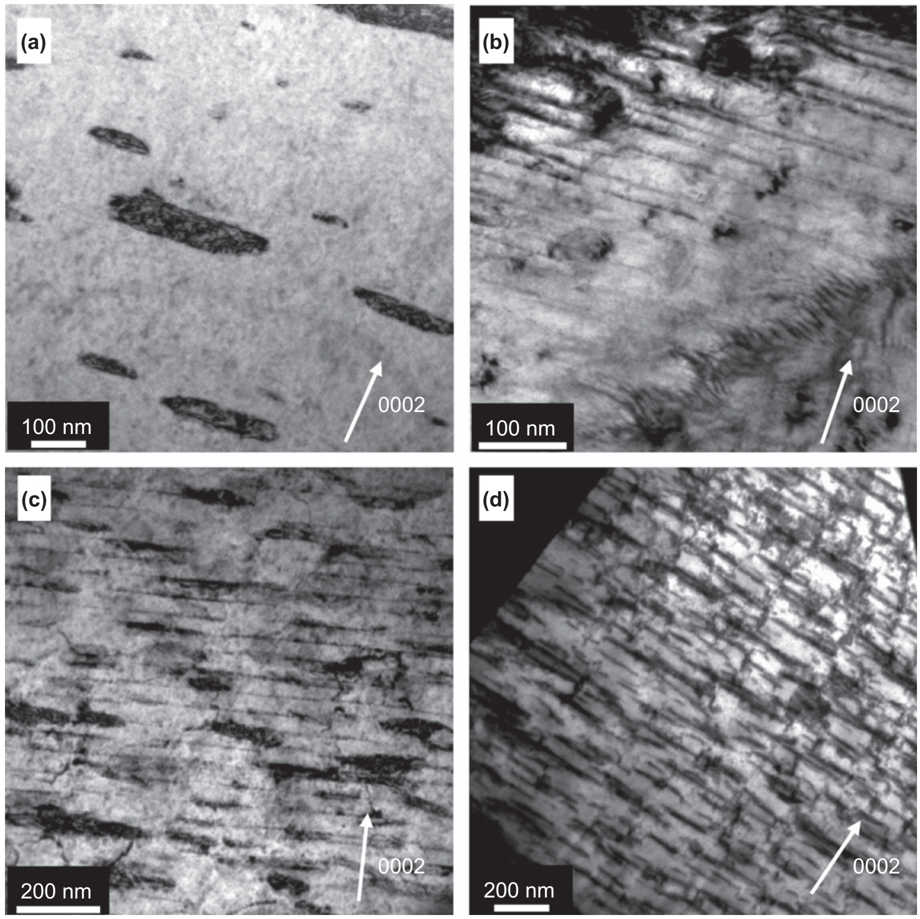

Fig. 3. BF-TEM images of pure Zr irradiated with self-ions at 673 K; (a) 5 dpa, (b) 15 dpa, (c) 20 dpa and (d) 40 dpa.

$\boldsymbol{g} \cdot \boldsymbol{b} = 0$, where $\boldsymbol{g}$ is the diffraction vector and $\boldsymbol{b}$ is the Burgers vector. Fig. 4a shows a BF-TEM image of pure Zr irradiated at 673 K to 20 dpa The dislocation contrast can be seen as parallel dark lines. The corresponding selected-area electron diffraction pattern is shown in Fig. 4d. The defect contrast forms inversely bright lines in the dark-field (DF) image when $\boldsymbol{g} = 0004$ was used (Fig. 4b), and the contrast disappears when $\boldsymbol{g} = 1\bar{1}00$ is used (Fig. 4c). The candidate Burgers vectors of the c-component dislocations are $1/6 < 11\bar{2}3 >$ and $1/2[0001]$; accordingly, $\boldsymbol{b}$ is determined to be $1/2[0001]$ since only this vector satisfies $\boldsymbol{g} \cdot \boldsymbol{b} = 0$. On the consideration described here, we have confirmed that the c-component dislocations formed by neutron irradiation can be simulated by self-ion irradiation not only from the viewpoint of the appearance of the microstructures but also from the crystallographic viewpoint.

Fig. 5 shows a TEM image of pure Zr irradiated with self-ions at 573 K to 20 dpa. This irradiation induced only dislocations that were entangled with hydrides and dislocation loops (about 100 nm in diameter), and a regular alignment of dislocations was not observed. The appearance of the microstructure is completely different from that of the microstructure obtained by irradiation at the higher temperature (673 K), as shown in Fig. 4, despite the damage level of 20 dpa being the same. This result suggests that the irradiation temperature affects the formation of c-component dislocation structures and that a high temperature is essential to form the damage structures.

Fig. 6a shows a BF-TEM image of Zircaloy-2 irradiated with self-ions at 573 K to 20 dpa. In spite of the same irradiation conditions as those in Fig. 5, c-component dislocation structure was observed in contrast to the case of pure Zr. Burgers vector analysis was carried out using $\boldsymbol{g} = 0004$ and $1\bar{1}00$ reflections, similarly to the case shown in Fig. 4. The defect contrast appeared in the DF image when $\boldsymbol{g} = 0004$ was used (Fig. 6b) but it disappeared when $\boldsymbol{g} = 1\bar{1}00$ was used (Fig. 6c). Accordingly, the Burgers vector was determined to be $1/2[0001]$. Comparing Zircaloy-2 with pure Zr, it is considered that the presence of alloying elements promotes the formation of c-component dislocation structures.

The distribution of c-component dislocations lying on the basal plane was investigated. Fig. 7a shows a DF-TEM image of Zircaloy-2 irradiated with self-ions at 573 K to 20 dpa. The image was taken under the conditions ensuring that the direction of incident electrons was slightly oblique to the basal plane as schematically shown in Fig. 7b. Similarly to the case of neutron irradiation, dislocation loops were observed on the inclined plane with an elliptical shape and a diameter of 10–20 nm. It was found that the loops were homogeneously formed on the basal plane.

4. Discussion

The present study has revealed the effects of the dpa value, the irradiation temperature and the presence of alloying elements on the formation of c-component dislocation structures in pure Zr and Zircaloy-2. The obtained results are summarized in Table 3.

As shown above, in the case of 20 dpa irradiation, c-component dislocation structures were formed in pure Zr at 673 K (Figs. 3c and 4) but not at 573 K (Fig. 5). This shows that vacancies become mobile at high temperatures. The rate of vacancy aggregation may increase with temperature increasing, and vacancy clusters

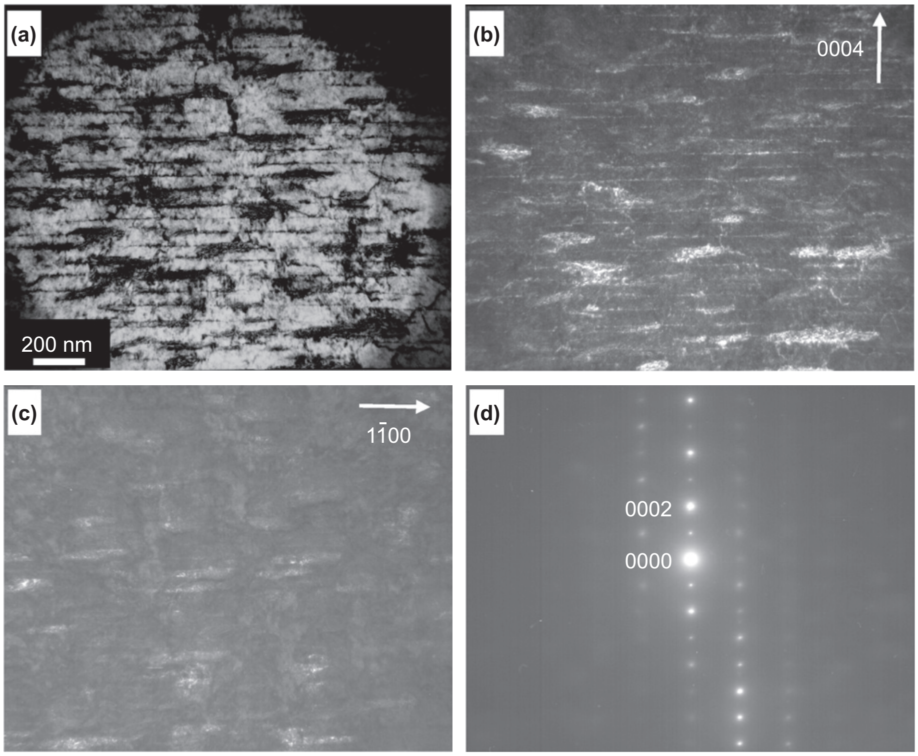

Fig. 4. (a) BF and (b and c) DF-TEM images of pure Zr irradiated with self-ions at 673 K to 20 dpa. (d) Corresponding selected-area diffraction pattern.

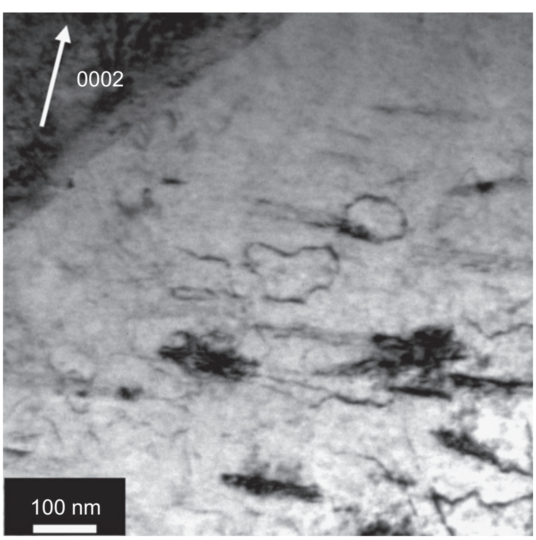

Fig. 5. BF-TEM image of pure Zr irradiated with self-ions at 573 K to 20 dpa.

form c-component dislocation loops. This growth mechanism of c-component dislocation loops is consistent with the model proposed by Lee and Koch [9]. They studied the temperature dependence of the formation of damage structures in Zircaloy-2 and showed that c-component dislocation structures are formed by irradiation with Ni ions at 673 and 773 K but not at a lower temperature (573 K). The temperature dependence of the formation of c-component dislocation structures in high-purity Zr irradiated with neutrons was reported by Jostsons et al. [11]. They showed that under the irradiation with fluence 1.3×10^{25} nm^{-2} (neutron energy $E > 1.0$ MeV) (corresponding to about 3 dpa according to the relationship 10^{25} nm^{-2} = 2 dpa [12]), c-component dislocation structures are formed at 723 and 773 K but not at 673 K. These results reported on temperature dependence qualitatively agree with our results that under the self-ion irradiation, c-component dislocation structures were formed in pure Zr at 673 K but not at the lower temperature of 573 K in pure Zr.

Our results also indicate that the presence of alloying elements (Sn, Fe, Cr and Ni) promotes the formation of c-component dislocation loops. The alloying elements may have an effect on the accumulation of vacancies, similar to the attracting interaction between vacancy and impurity atoms confirmed to occur in various metals [13,14]. However, the relationship between the sites of the alloying elements and the formation of c-component dislocation loops is unclear. We consider that small precipitates (clusters) exist and act as sinks for vacancies. Griffiths et al. studied the microstructures of Zircaloy-2 and crystal-bar Zr irradiated with neutrons [15]. They showed that even under the same irradiation conditions (745 K, 1.08×10^{25} nm^{-2} ($E > 1.0$ MeV) (corresponding to about 2 dpa)), c-component dislocation structures were formed in Zircaloy-2 but not in crystal-bar Zr. Similarly to our results, this also suggests that the presence of alloying elements affects the formation of c-component dislocation structures.

In addition to self-ion irradiation, we observed Zircaloy-2 irradiated with neutrons at burn-up values of 30 and 60 MWd/kgU as shown in Fig. 8. The materials were irradiated in a European commercial BWR and were sequentially subjected to a ramp test carried out at the Halden test reactor. The irradiation temperature was about 573 K. Both images (Fig. 8a and b) show c-component dislocation structures and there is a strong similarity between them (i.e., linear contrast and dislocation spacing). No clear burn-up dependence of the damage structures was observed. It is estimated that the burn-up values of 30 and 60 MWd/kgU correspond to damage levels of 11 and 22 dpa, respectively, based on the equation 50 MWd/kgU = 18 dpa [12]. Accordingly, the TEM images of Fig. 8 may be quantitatively compared with those of Fig. 3b and c as the dpa values are almost the same. We can confirm that the damage structures formed by the irradiation with neutrons or

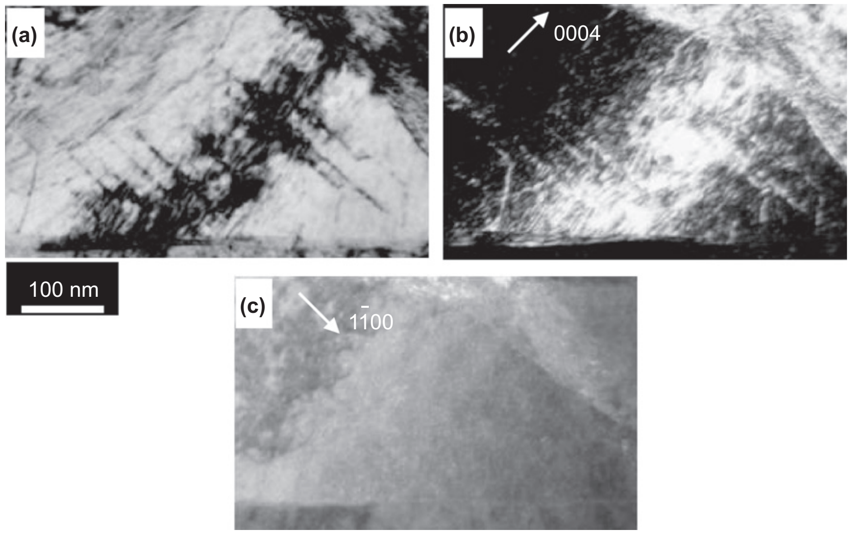

Fig. 6. (a) BF and (b and c) DF-TEM images of Zircaloy-2 irradiated with self-ions at 573 K to 20 dpa.

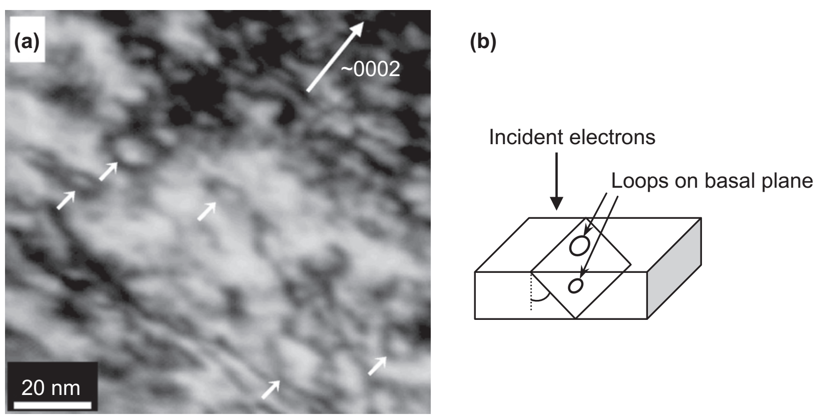

Fig. 7. (a) DF-TEM image of Zircaloy-2 irradiated with self-ions at 573 K to 20 dpa. Dislocation loops are indicated by small arrows. (b) Schematic view of the observation.

Table 3
Formation of c-component dislocation structures in pure Zr and Zircaloy-2 by self-ion irradiation under various conditions.

Material	Temperature (K)	Damage (dpa)	Formation of c-component dislocation structures
Pure Zr	573	20	No
Pure Zr	673	5	No
Pure Zr	673	15	Yes
Pure Zr	673	20	Yes
Pure Zr	673	40	Yes
Zircaloy-2	573	20	Yes

self-ions are the same at the same dpa value. Furthermore, there is no clear dependence on burn-up for the appearance of the c-component dislocation structures in the observed damage range in the case of both neutron (corresponding dpa values are 11 and 22 dpa) and self-ion irradiation (15 and 20 dpa).

It should be noted that the peculiar dislocation structure shown in Fig. 3d with discontinuous segments rather than linear contrast was formed only under irradiation with a comparatively high level of damage (40 dpa). The peculiar contrast indicates that the regular alignment of the c-component dislocations has been modified. It is probable that the ordered c-component dislocations are formed only within a specific damage range.

In addition to zirconium hydrides, intermetallic compounds of $Zr(Fe,Cr)_2$ and $Zr_2(Ni,Fe)$ are also typical precipitates in Zircaloy-2. It is known that neutron irradiation amorphizes $Zr(Fe,Cr)_2$ and subsequently causes an irradiation-induced solid solution of Fe and Cr [16]. A change in the elemental distribution is thought to affect the ductility of Zr-base alloys but its mechanism is not clear. Self-ion irradiation should be one of the efficient methods to elucidate this mechanism.

Fig. 9 shows a-component dislocation loop structure in Zircaloy-2 specimen that was neutron-irradiated in the commercial BWR under the irradiation conditions (573 K, 30 MWd/kgU). The Zircaloy-2 specimen was obtained from the same material shown in Fig. 8b. The loops are found to be 5–10 nm in diameter. This TEM specimen was prepared by electropolishing instead of FIB milling. Unfortunately we were not able to identify a-component dislocation loops in FIB milling specimens of pure Zr or Zircaloy-2 irradiated with self-ions. Since the FIB milling process for preparing thin foils produced dot-like contrast similar to the a-component dislocation loops in both the unirradiated and irradiated specimens, it was too difficult to distinguish between the dot-like contrast and the a-component dislocation loops. As already mentioned, we recognize that the c-component dislocations are empirically related to the ductility degradation in the cladding with high fluence, so we do not continue to investigate a-component dislocation loops further here.

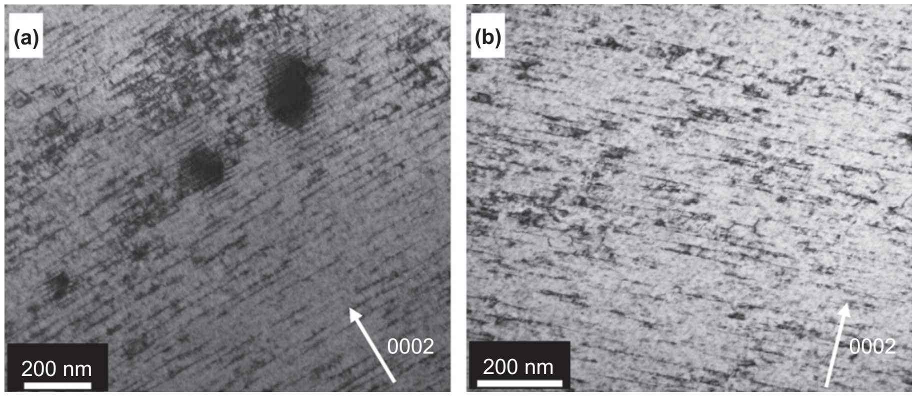

Fig. 8. BF-TEM images of neutron-irradiated Zircaloy-2. (a) 60 MWd/kgU (≒22 dpa) and 573 K, (b) 30 MWd/kgU, (≒11 dpa) and 573 K.

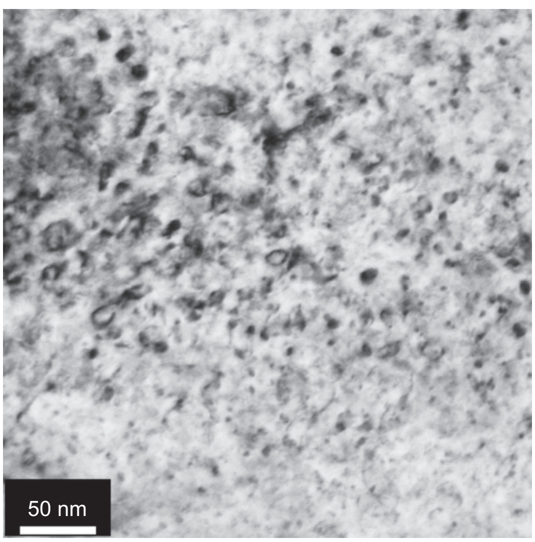

Fig. 9. BF-TEM image of a-component dislocation loop structure in Zircaloy-2 neutron-irradiated in the commercial BWR (573 K, 30 MWd/kgU).

The results presented here show the validity of the use of self-ion irradiation to elucidate microstructural changes in pure Zr and Zircaloy-2 under neutron irradiation conditions. The self-ion irradiation technique is also useful since it is not necessary to handle the irradiated specimens as radioactive materials when observing or analyzing them. Finally, it should be noted that such a high level of damage (40 dpa) is not easily attainable using neutron source facilities or material test reactors. Accordingly, this simulation technique is efficient for developing cladding materials tolerant to high burn-up.

5. Conclusions

The self-ion irradiation technique for pure Zr and Zircaloy-2 has been developed to simulate c-component dislocation structures formed in neutron-irradiated Zircaloy-2. The damage structures formed by self-ion and neutron irradiation are the same from the viewpoint of not only the appearance of the microstructures but also the crystallography (Burgers vector of 1/2[0001]). We found that the formation of c-component dislocation structures depends on the irradiation temperature and damage level. In pure Zr, when the irradiation temperature is low (573 K), damage structures are not formed even at a high level of damage (20 dpa). On the other hand, at higher irradiation temperature (673 K), damage structures are formed at damage levels of 15, 20 and 40 dpa. The c-component dislocation structures are formed in Zircaloy-2 at 573 K and 20 dpa, whereas they are hardly formed in pure Zr under the same irradiation conditions. These results suggest that the presence of alloying elements promotes the formation of the c-component dislocation structures. The self-ion irradiation technique is expected to be useful for the study of irradiation damage in various materials. In contrast to neutron irradiation, test conditions such as dpa values and temperatures can be precisely controlled, moreover, ion irradiation can realize a high level of damage in a comparatively short time. This simulation technique should be effective for developing cladding materials for LWRs.

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