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Original Article

EFFECTS OF ION IRRADIATION ON MICROSTRUCTURE AND PROPERTIES OF ZIRCONIUM ALLOYS—A REVIEW

CHUNGUANG YAN [a], *RONGSHAN WANG* [b], *YANLI WANG* [a,*], *XITAO WANG* [a], *and GUANGHAI BAI* [b]

[a] *State Key Laboratory for Advanced Metals and Materials, University of Science and Technology Beijing, 30 Xueyuan Road, Haidian District, Beijing 100083, People's Republic of China*

[b] *Life Management Technology Center, Suzhou Nuclear Power Research Institute, 1788 Xihuan Road, Jinchang District, Suzhou 215004, People's Republic of China*

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A B S T R A C T

Zirconium alloys are widely used in nuclear reactors as structural materials. During the operation, they are exposed to fast neutrons. Ion irradiation is used to simulate the damage introduced by neutron irradiation. In this article, we briefly review the neutron irradiation damage of zirconium alloys, then summarize the effect of ion irradiation on microstructural evolution, mechanical and corrosion properties, and their relationships. The microstructure components consist of dislocation loops, second phase precipitates, and gas bubbles. The microstructure parameters are also included such as domain size and microstrain determined by X-ray diffraction and the S-parameter determined by positron annihilation. Understanding the relationships of microstructure and properties is necessary for developing new advanced materials with higher irradiation tolerance.

1. Introduction

Zirconium and its alloys exhibit a low thermal neutron absorption cross-section, good corrosion resistance in high-temperature and high-pressure steam or water, and adequate mechanical properties. These alloys are therefore widely used as cladding and guide tubes in pressure water reactors. As one of the most important safety barriers, cladding tubes are not only used to encapsulate nuclear fuel, but also to prevent the nuclear fission product from leaking [1].

For a long service period, the microstructure and properties of zirconium alloys change gradually in the harsh in-pile environment including water, stress, corrosion medium, and intense neutron irradiation. Irradiation damage, for example, irradiation growth is a main concern because it influences the structural integrity of reactors [2]. The entire testing process of the neutron irradiation of materials is

* *Corresponding author.*
E-mail address: wangyl@ustb.edu.cn (Y. Wang).

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long and expensive. Even after neutron irradiation, it is difficult to study samples with residual radioactivity unless with special facilities. Simulation of neutron irradiation damage with ion irradiation is necessary to give an insight into the irradiation effects of zirconium alloys. The ion irradiation test is shorter in time, higher in efficiency, lower in cost, and an easy-to-handle process [3], and the topic of ion irradiation of zirconium is of great interest to researchers. This article gives a short description of neutron irradiation of zirconium alloys firstly, and then pays more attention to microstructural evolution, mechanical and corrosion properties of zirconium alloys induced by ion irradiation. Meanwhile, their corresponding mechanisms are discussed.

2. Neutron irradiation effects

Irradiation damage is a process in which primary knock-on atoms (PKAs) induced by energetic particles' bombardment with the target material come to rest in the crystal lattice as an interstitial, which involves the creation of point defects and defect clusters. The irradiation effects are the result of the evolution of these defects, aggregation or dissolution, causing changes in physical and mechanical properties [4]. Under neutron irradiation, materials degradation becomes obvious, which are classified as physical effects and mechanical effects [5].

Different kinds of point defects and defect clusters are produced in the irradiation process [6]. The grain boundary and interfaces serve as effective sinks for these defects [7]. The coupling between defects fluxes and alloying elements fluxes results in enrichment or depletion of alloying elements near the grain boundary and interfaces. This is called radiation induced segregation [8]. It is clear that Fe element concentration gradient near the precipitates/matrix boundary, changes more obviously due to its higher diffusion ratio as compared to other elements in Zr-2, such as Sn, Cr, and Ni [9]. Dislocation loops are typical point-defect clusters in irradiation-induced cascades [10]. In zirconium alloys, <a>-dislocation loops are either interstitial-type or vacancy-type loops situated in the prismatic planes of the hexagonal close-packed (hcp) lattice with Burgers vector $\mathbf{b}=1/3\langle 11\bar{2}0\rangle$ or equivalent, which appears at a low neutron dose. High temperature and work hardening would accelerate their saturation in Zr-2, Zr-4, and Zr-2.5Nb [11]. The ratio of vacancy-type loops to interstitial-type loops depends on the irradiation temperature. The <c>-dislocation loops are vacancy-type loops formed in the basal planes with Burgers vector $\mathbf{b}=1/2\langle 0001\rangle$ or $\mathbf{b}=1/6\langle 20\bar{2}3\rangle$, which can only be observed above critical dose, and influenced by the chemical composition [12–14], work hardening [10], and irradiation temperature [10,11]. For second-phase precipitates (SPPs), they are observed in various advanced zirconium alloys such as Zircaloy series and Zirlo (United States) [15], E635 and E110 series (Russia) [16], M5 (France) [17], and HANA series (South Korea) [18]. These SPPs exhibit microstructural evolution when exposed to neutron irradiation. In Zr-2 and Zr-4 alloys under certain neutron irradiation doses, the precipitates $Zr(Fe,Cr)_2$ and $Zr_2(Fe,Ni)$ transform to an amorphous state at low irradiation temperature (< 350 K) [19,20], then the $Zr(Fe,Cr)_2$ precipitates transform to an amorphous phase while the $Zr_2(Fe,Ni)$ precipitates partially dissolve and remain crystalline at medium temperatures (520–600 K) [10,19,21], and both maintain crystalline at high temperatures (640–710 K) [20]. The $Zr(Nb,Fe)_2$ precipitates transform to β-Nb under irradiation in Zr-1Nb-0.1Fe alloys at about 620 K [16].

The aforementioned microstructural evolution has an inevitable effect on mechanical and corrosion behavior. The uniform corrosion is enhanced while the nodular corrosion resistance of neutron irradiated Zr-2 is improved due to the neutron irradiation [22]. Considering the mechanical effects, the zirconium alloys exhibit irradiation hardening [23,24], irradiation growth [2,25,26], and reduction of plastic anisotropy [27,28].

It can be observed that in the harsh service environment, the neutron irradiation plays an important role in microstructural evolution and mechanical properties changes of zirconium alloys. This makes the component degradation modes in reactors more complex. It is wise to evaluate the factors involved in the degradation modes by the single-parameter method. The simulation of neutron irradiation damage by ion irradiation offers a much better way to study the irradiation damage.

3. Irradiation-induced microstructural evolution

The simulation of in-pile neutron irradiation damage by out-of-pile ion irradiation is based on their comparable physical and mechanical effects. Ion irradiation damage has several strengths when compared to neutron irradiation: several years' in-pile test period is shortened to a few hours or less due to its high damage rate; irradiation induced activation can be avoided; the experimental parameters can be controlled precisely; the PKA energy induced by the ions is comparable to the one induced by neutrons; and the overall process is economical. However, the damage range is non-uniform and the region is limited to several millimeters or hundreds of nanometers. The bulk properties are therefore difficult to determine through conventional technique [3]. The following content mainly focuses on the microstructural evolution, mechanical and corrosion behavior induced by ion irradiation in zirconium alloys.

3.1. *<a>-Dislocation loop and its formation mechanisms*

The evolution of point defect clusters during irradiation has been studied extensively over the years. When the energetic particles bombard the target material, cascade collisions occur. Point defects are produced and aggregate into clusters. Lee and Koch [29] firstly studied the defects evolution of Ni ion irradiated Zr-2 alloys, but the exact type of those defects is not characterized in that study.

<a>-Dislocation loops, especially those induced by ion irradiation, are seldom distinguished between vacancy and

interstitial ones in these studies due to their very small size. Because of the production bias, the coexistence of both interstitial and vacancy loops are introduced at the end of the cascade relaxation [30]. That is to say, when the vacancy and interstitial clusters are produced in the cascade collisions, they can evolve into large loops at the same time.

The nucleation and growth of <a>-dislocation loops are influenced by the alloying elements, irradiation temperature, and dose. Hellio et al. [31] studied the effect of alloying elements on Zr^{+} ion irradiated α-Zr. Usually, the atoms of alloying elements provide preferential sites. Both substitutional Nb and interstitial O increase the density of this type of loops, but the O decreases the growth speed. While the mean size and density of these <a>-dislocation loops increase with the dose, the density decreases with increases in irradiation temperature. Higher irradiation temperature prompts the migration of point defects, so the point defects aggregate into bigger clusters or loops and the corresponding density decreases under certain irradiation doses. The *in situ* experiments of 1 MeV Kr ion irradiated M5 alloys at 573 K by Hengstler-Eger et al. [32] and pure zirconium at 573–773 K by Idrees et al. [33] show a similar evolutionary trend of <a>-dislocation loops.

3.2. <c>-Dislocation loop and its formation mechanisms

It is reported that the two types of dislocation loops are responsible for irradiation growth. The emergence of <c>-dislocation loops is closely related with the breakaway irradiation growth [34], and most studies focus on its evolutionary behavior. The nucleation and distribution of <c>-dislocation loops in a matrix of zirconium alloys show different features compared to <a>-dislocation loops.

Their nucleation occurs above a threshold dose, which is dependent on a critical interstitial solute concentration in the matrix [30]. Idrees et al. [33] show that both alloying elements and stress gradients of alloys have an important effect on their nucleation. At high temperatures, more solute impurities are dispersed into the matrix and lower the stacking fault energy of Zr. Meanwhile, during ion irradiation, segregation is observed. It is reported by Zou et al. [35,36] that Fe diffuses from the SPPs to the matrix in zirconium alloys when exposed to 1.5 MeV Ar ion irradiation, and this tendency is enhanced by the high temperature. Based on the inverse Kirkendall effect mechanism, the segregation is induced by the gradient of point defects near the sinks [37]. This irradiation induced redistribution of alloying elements changes the mixing enthalpy and mismatch entropy in the local area [38]. On one hand, the energy shift might have a positive effect on the nucleation. On the other hand, the mismatch influences the local stress. The nucleation of <c>-dislocation loops relieves the stress.

The threshold dose is related to the irradiation temperature and alloying elements, as is showed in Fig. 1. It can be seen that for pure Zr irradiated at 673 K and 773 K, the threshold doses are 0.8 dpa and 1.0 dpa [33]. For irradiated M5 alloy, its critical dose at 573 K is 6.8 dpa [32]. For irradiated Zr-Excel alloy (Zr-3.5Sn-0.8Mo-0.8Nb), the value at 673 K is 2.5 dpa [39]. According to these studies, four points should be noted here to state the parameters influence on the nucleation and distribution of <c>-dislocation loops as follows:

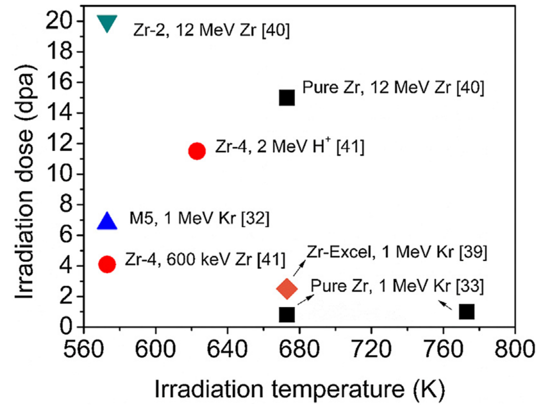

Fig. 1 – The threshold irradiation dose reported with corresponding irradiation temperature for zirconium alloys.

(1) Effect of alloying element

As discussed previously, the alloying elements in the matrix of Zr assist the nucleation of <c>-dislocation loops. Yamada and Kameyama [40] have irradiated pure zirconium and Zr-2 alloys with 12 MeV Zr ions at 573 K up to 20 dpa. It can be found that <c>-dislocation loops appear in Zr-2 alloys but not in pure zirconium. This result confirms that alloying elements of Sn, Fe, Cr, and Ni promote the accumulation of vacancies. But from Fig. 1, it can also be observed that for pure Zr and Zr-Excel irradiated with 1 MeV Kr at 673 K, the threshold dose for Zr-Excel is higher than pure Zr. The possible reason is that alloying elements have different effect on the formation of <c>-dislocation loops. The exact effect of alloying element on its formation is still unclear up to now.

(2) Effect of irradiation temperature

Yamada and Kameyama [40] also studied the effect of irradiation temperature on the nucleation of <c>-dislocation loops in irradiated pure zirconium with 12 MeV Zr ions at 573 K and 673 K. When the irradiation temperature is 573 K, <c>-dislocation loops are absent in a matrix irradiated up to 20 dpa. When it rises to 673 K, the <c>-dislocation loops appear. This result indicates that a high temperature is essential for the nucleation of <c>-dislocation loops. The high temperature irradiation is more complex due to the thermal stress relaxation. Idrees et al. [33] revealed that the stresses generated during ion irradiation are lowered due to the high temperature stress relaxation. The stress that assists the formation of <c>-dislocation loops is reduced, so the critical dose of their nucleation is higher for 773 K irradiation when compared to 673 K irradiation.

(3) Effect of ion species

Different types of ions with a variant energy from hundreds of keV to several MeV have been used to study irradiation induced microstructural evolution. The most used ion species are protons, noble gas ions, and Zr ions. The <c>-dislocation loops appear in Zr-4 alloys subjected to 600 keV Zr ions and 2 MeV protons. For Zr irradiation, above the critical dose of about 2.9 dpa, their mean diameter of <c>-dislocation loops range from 24 nm to 36 nm, much smaller than the ones induced by neutron irradiation, whose mean diameter is about 150 nm. For proton irradiation, their mean diameter is about 123 nm, which is much closer to the ones induced by neutron irradiation [41]. From the view of the damage dose rate, dislocation loops produced by energetic particles with a higher damage rate, is smaller with a higher density. In the research [41], the damage rate of Zr ion and proton irradiation is 7,000 and 200 times larger than neutron irradiation, which is about 7.29×10^{-8} dpa/s. The irradiation with high-dose rate tends to introduce a high density of small dislocation loops.

(4) Effect of sinks

The grain boundary, precipitate/matrix interface, and free surface serve as sinks for point defects, so the distribution of <c>-dislocation loops near these sinks is different. For 2 MeV proton irradiated Zr-4 at 623 K, a higher density of dislocation loops near the precipitates can be observed. The reason is that the Fe segregates from precipitates to matrix, the alloying element assists the nucleation of dislocation loops [41]. For the distribution around the grain boundary, the denuding of <c>-dislocation loops are observed in both 1 MeV Kr irradiated pure Zr up to 1 dpa at 773 K and Zr-Excel up to 10 dpa at 373 K. From the energy-dispersive X-ray spectroscopy line scan analysis, there exists a Fe depletion zone near the grain boundary [33,39]. For preexisting dislocations, they act as preferential sinks and increase the probability of defect clustering. From the aforementioned discussions, it can be found that the nucleation of <c>-dislocation loops is closely related with Fe element distribution. The sinks have different effects on the segregation of Fe, so the depletion or enrichment of <c>-dislocation loops occurs.

3.3. *SPPs phase evolution and their mechanisms*

The precipitates have a great effect on the corrosion behavior of zirconium alloys. The phase transformation under ion irradiation is a topic of great interest to material researchers.

The ion irradiation accelerates the dissolution of precipitates, prompts the phase transformation, coarsens the precipitates, and induces the formation of a new phase. Kai et al. [42] studied the 1 MeV proton irradiated Zr-4 alloy with damage dose up to 1 dpa at 623K. After the postirradiation examination, it was found that the $ZrFe_2$ precipitates are dissoluted, $Zr(Fe,Cr)_2$ precipitates transform from hcp (C14) to fcc (C15), and the Zr_4Sn precipitates nucleate and grow.

In recent years, special attention has been paid to the phase transformation of $Zr(Fe,Cr)_2$ precipitates [19, 43–48], and the results are summarized in Fig. 2. From this figure, the factors influencing the amorphization behavior can be drawn as follows.

(1) Effect of irradiation temperature and dose

It can be seen that when the irradiation temperature is about 100 K, the damage dose of amorphization of precipitates is about 1 dpa. Compared to the high temperature irradiation, take Ar irradiation at 770 K up to 11 dpa, for example; they still remain crystalline, as shown in Fig. 2. Swanson et al. [49] showed that the formation of amorphous structures by ion irradiation results from the defect accumulation. That is to say, the defects accumulate as the irradiation process continues. Amorphization occurs until the defect concentration reaches the critical level required for spontaneous transformation to amorphism. At low temperature, the annealing of these defects is little; their concentration can reach a relatively high level with increased doses. When the concentration is above the threshold value, the crystalline structure transforms to the amorphous one. At higher temperatures, the thermal annealing is pronounced, so the irradiation dose of amorphization is high accordingly [50]. It should be noted that in Fig. 2 the data points in the dashed circle represent that the precipitates state is amorphous or partially amorphous [45]. The defects are accumulated with continuous doses, and finally the amorphization of these precipitates are observed.

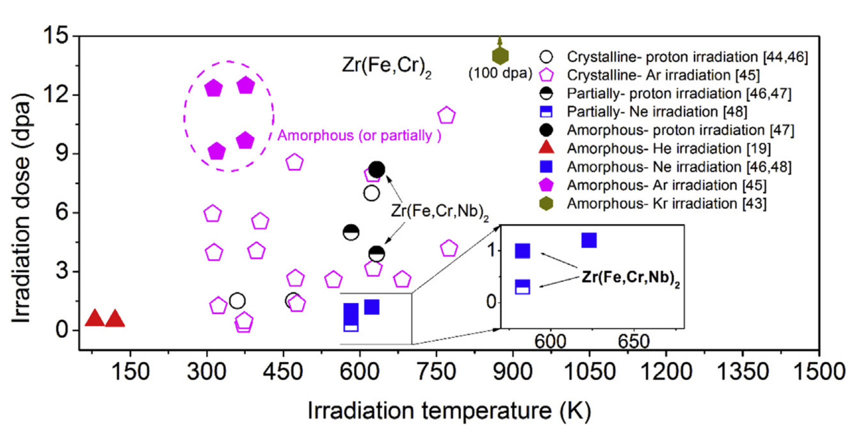

Fig. 2 – Irradiation dose to amorphization under ion irradiation as a function of irradiation temperature for $Zr(Fe,Cr)_2$ precipitates.

(2) Effect of alloying element

The alloying element has an effect on the irradiation behavior of these precipitates. In Fig. 2, Zu et al. [46] found that $Zr(Fe,Cr)_2$ precipitates in Zr-4 alloy exposed to 600 keV Ne ions up to 1.2 dpa transform from crystalline to amorphous partly at 623 K. Although the same precipitates under proton irradiation up to 7 dpa at the same temperature are still crystalline. Shen et al. [47,48] have studied the $Zr(Fe,Cr,Nb)_2$ precipitates in Zr-1.6Sn-0.6Nb-0.2Fe-0.1Cr alloy irradiated by 2 MeV proton at 633 K and 500 keV Ne at 583 K. The amorphization of precipitates starts at 3.9 dpa and at 8.2 dpa, they are completely amorphous. It is believed that a higher damage dose is necessary for amorphization at higher irradiation temperatures. The comparison between doses of 3.9 dpa for partial amorphization at 633 K, to the dose of 7 dpa for complete crystalline at 623 K, shows that the addition of Nb in the precipitates is harmful to the irradiation resistance of the precipitates.

(3) Effect of ion species

Generally, there are two models used to explain the irradiation induced amorphization: the direct-impact model and the defect accumulation model. Like the liquid alloy quenching, the direct-impact model assumes the amorphization happens in the core of cascade displacement. The defect-accumulation model supposes that the amorphization appears when the local defect density reached a threshold level. During the cascade displacements, the main cascades split into smaller cascades [51]. For heavier ion irradiation, the critical temperature is higher and the crystallization efficiency is lower [52].

In addition to those models, Naguib and Kelly [53] believed that the crystalline to amorphous transformation is influenced by the ionicity and the ratio of crystallization to the melting point. In the bond-type field, when the ionicity is $\leq$ 0.47, the amorphization occurs. In the temperature field, this happens when the ratio is $\geq$0.30. Brimhall et al. [54] showed that the solubility criterion can be used to predict the amorphization of intermetallic compounds. The compounds with no or lower solubility go through a higher increase in free energy. The higher the free energy, the less stable the intermetallic compounds. During the irradiation, the compounds have a greater probability to transform to an amorphous state. Some research also showed that the ability of amorphization is closely linked with glass formation. A material with a greater glass formation ability exhibits a good tendency for amorphization [55,56].

3.4. *Statistical parameters for microstructural evolution*

The transmission electron microscopy has provided a direct observation of microstructural evolution induced by irradiation. Other characterization techniques, such as X-ray diffraction and positron annihilation techniques, have also been used to study the microstructural evolution of ion irradiated zirconium alloys.

(1) X-Ray diffraction technique

During the X-ray diffraction line profile analysis, the line broadening results from the instrument, the small particle size, and the microstrain. The profiles are fitted by different profile shape functions [57], and this just changes the form of broadening equations. The microstrain and domain size are characterized by analyzing the integral breadth change of peaks subtracting the instrumental breadth. Mukherjee et al. [58–62] have paid more attention to the change of Zr-1Nb-1Sn-0.1Fe alloys under 15 MeV proton, 116 MeV O^{5+} ion and 145 MeV Ne^{6+} ion irradiation, and Zr-1Nb under 116 MeV O^{5+} ion irradiation. For Zr-1Nb-1Sn-0.1Fe, it can be found that the domain size, microstrain, and density of dislocation does not change obviously even up to the highest dose under proton irradiation compared to the unirradiated one. But for the heavy ion irradiation, the microstrain and density of dislocation increase and the domain size decreases with the irradiation dose. When the generation of point defects dominates the annihilation, the density of dislocation and microstrain increases with dosage. The domain size decreases are because of the formation of a dislocation substructure. For Zr-1Nb, there exists a sharp decrease in microstrain and density of dislocations at the dose of 2×10^{18} O^{5+}/m^2. The reason is that the dislocations introduced by the irradiation serve as sinks for the subsequent point defects, so the annihilation of point defects dominates the generation.

(2) Positron annihilation technique

The positron annihilation technique is a powerful tool to study the vacancy-type defects induced in the irradiation process. For ion-irradiated zirconium alloys, variable-energy positron energy beams are used to study the defect density as a function of penetration depth [32,63]. The S-parameter is defined as the ratio of central area (around 511 keV) to total peak intensity, reflecting the annihilation with low momentum electrons. There are vacancies and voids in irradiated alloys which resulte in a higher S-parameter value compared with unirradiated alloys. For Ar irradiated Zr-4, the S-parameter increases with the dose, but for heavier Zr ion irradiated M5 up to 0.3 dpa, the S-parameter doesn't change significantly. The vacancies introduced by heavier ion irradiation are balanced by their recombination and reach a high density even at a low dose. After annealing, the vacancies are annihilated, and the S-parameter decreases with the annealing temperature.

3.5. In-situ *annealing behavior*

This section mainly reviews the *in-situ* annealing behavior of ion irradiated zirconium alloys. The microstructural evolution of <c>-dislocation loops, $Zr(Fe,Cr,Nb)_2$ precipitates and Kr bubbles reported in references are summarized here.

(1) <c>-Dislocation loops

Hengstler-Eger et al. [32] studied the annealing behavior of M5 alloy irradiated up to 22 dpa from 753 K to 1023 K. The density of dislocation loops decreases with irradiation temperature. At higher temperatures, these dislocation loops migrate to anneal and transform into dislocation lines.

(2) $Zr(Fe,Cr,Nb)_2$ precipitates

Shen et al. [48] studied the recrystallization of $Zr(Fe,Cr,Nb)_2$ precipitates irradiated up to 6.1 dpa at temperatures from 373 to 973 K. The recrystallization starts at 723–873 K. The amorphous to crystalline transformation involves the rearrangement of alloying element and dissipation of vacancies to matrix.

(3) Kr bubbles

When the damage dose is large enough, the inert gas ions aggregate in the matrix. The Kr bubbles form when the content exceeds the solubility of the gas in the alloys [64]. Ran et al. [65] studied the growth behavior of Kr bubbles in Zr-1.1Nb-1.51Fe-0.26Cu-0.72Ni irradiated up to 63.4 dpa. For the irradiated alloys, the gas bubbles increase with annealing time and temperature. According to the activation energy of coarsening of about 0.319 eV determined, the growth mechanism is controlled by the surface diffusion.

4. Postirradiation properties

4.1. *Mechanical properties*

From the aforementioned results, it can be found that the dislocation loops, bubbles, and sometimes new precipitates are introduced by ion irradiation. These microstructural components serve as obstacles to dislocation motivation, and the total hardening can be expressed as follows [66]:

$$\Delta\tau_{\mathrm{total}} = \left[\sum_{\mathrm{i}} (\Delta\tau_{\mathrm{i}})^2\right]^{1/2}$$

$$\Delta\tau_\rho = \alpha_\rho \mu b \sqrt{\rho}$$

$$\Delta\tau_\mathrm{b} = \alpha_\mathrm{b} \mu b \sqrt{N_\mathrm{b} d_\mathrm{b}}$$

$$\Delta\tau_1 = \alpha_1 \mu b \sqrt{N_1 d_1}$$

where $\Delta\tau_{\mathrm{total}}$ is total hardening, $\Delta\tau_\rho$, $\Delta\tau_\mathrm{b}$, and $\Delta\tau_\mathrm{l}$ are increases in shear stress due to the dislocation density ρ, gas bubbles density N_b and dislocation loops density N_l. α_ρ, α_b, and α_l are interaction parameters of dislocation-dislocation, dislocation-bubble, and dislocation-loop, respectively. d_b and d_l are the diameters of bubbles and loops. μ is the shear stress, and b is the Burgers vector. For the single ion beam irradiation, the hardening mechanism is easy to understand, as reported in He or Ar ion irradiated Zr-4 [67], as shown in Fig. 3A. Different ion species irradiation may have different hardening sources. With double-ion irradiation, for example, ΔH_A and ΔH_B are hardening effects of a single ion beam irradiation, if the two hardening sources are similar, their combined hardening is given by $\Delta H_\mathrm{R} = (\Delta H_\mathrm{A}^2 + \Delta H_\mathrm{B}^2)^{1/2}$. If their hardening sources are different, the hardening formula is $\Delta H_\mathrm{L} = (\Delta H_\mathrm{A} + \Delta H_\mathrm{B})$. Dayal et al. [67] also studied the hardening mechanism of double ion implantation by He and Ar. Their combined hardening value is between ΔH_L and ΔH_R, which is a mixture of similar and dissimilar hardening mechanisms.

The indentation creep measurement is used to simulate the creep at scratches [68]. For irradiated alloys, the slipping dislocations interacts with the irradiation defects, such as dislocation loops or bubbles, which turn out to the increase in the creep activation energy. The activation energy of Zr-2.5Nb increases with irradiation damage dose (Fig. 3B), because small dislocation loops in the microstructure induced by irradiation act as obstacles to dislocation gliding [68].

Irradiation growth is a dimensional change without stress, which is one of the most important factors limiting the lifetime of reactor components [2]. The irradiation growth simulated with ion irradiation has the advantage of the elucidation of mechanisms by the single-parameter method. It has been studied with cantilever beam specimens phenomenologically and does not give explanations from the microstructure point, which is affected by the alloy composition, texture, and grain shape [69–71]. It shows that the alloying elements depress the deflection at the free end of the cantilever. From the microstructural evolution just discussed, we can say that the alloying elements assist the nucleation of dislocation loops, and reduce their growth. The growth strain along the longitudinal direction is larger than the one along the

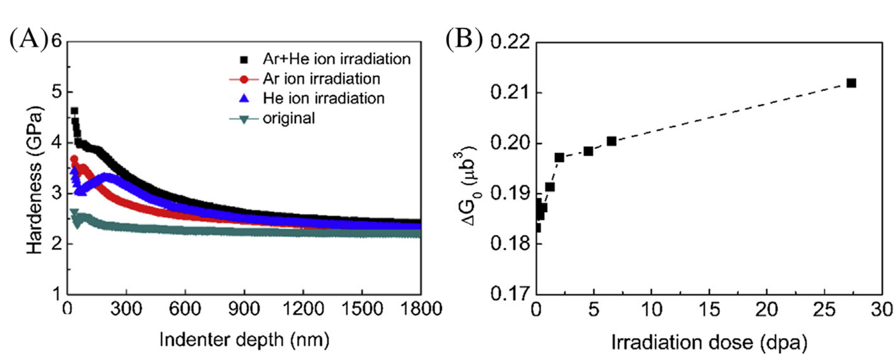

Fig. 3 – Mechanical effects of zirconium alloys under ion irradiation. (A) Irradiation hardening. (B) Irradiation induced increase of creep activation energy in indentation creep.

transversal direction. It can be explained that the anisotropy diffusion of point defects causes the elongation along <a> axis and shortening along <c> axis.

4.2. Corrosion properties

The corrosion properties consist of high temperature oxidation and electrochemical behavior. The high temperature oxidation of Zr ions irradiated Zr-4 alloys is enhanced with increased the irradiation dose. During high temperature oxidation of the irradiated Zr-4 alloys, on one hand, the point defects and dislocation loops induced by ion irradiation provide a fast diffusion channel to the oxygen atom. On the other hand, an electric field is formed to accelerate the movement of electrons from the surface to the matrix [72].

As discussed previously, the damage layer is thin due to the heavy ion irradiation. The electrochemical behavior is sensitive to the surface conditions, so it is used to evaluate the irradiation damage of zirconium alloys. The electrochemical behavior of Zr-4 alloys is influenced by the balance between irradiation damage and oxidation protection [73]. Considering the electrochemical properties, the protective surface of oxide layer ZrO_2 is destroyed by the bombardment of ions. The balance between irradiation damage and oxidation protection results in corrosion resistance from enhancement to saturation, and finally to decrement stage in H_2SO_4 water solution [73–75].

5. Conclusions

Ion simulation of neutron irradiation of zirconium alloys has been studied for many years. In the current article, the microstructural evolution, mechanical and corrosion properties, and corresponding relationships induced by ion irradiation are summarized as follows:

(1) Ion irradiation damage can be used to simulate the damage induced by neutron irradiation. In addition, it provides more flexibility to study the influence factors by the single-parameter method.
(2) The dislocation loops are main defects produced during the irradiation. For <a>- and <c>-dislocation loops, their size increases with irradiation temperature and irradiation dose. The alloying elements provide preferential sites for their nucleation, but their effect on the growth is unclear, especially for <c>-dislocation loops. The nucleation of <c>-dislocation loops is more complicated. It is also affected by the stress in the matrix. The distribution of <c>-dislocation loops is special around the grain boundary, free surface, and preexisting dislocation line, which serve as sinks for point defects.
(3) The transformation from crystalline to amorphous of the $Zr(Fe,Cr)_2$ precipitates under ion irradiation has been studied extensively. The transformation is accompanied by Fe depletion in the amorphous region and affected by the irradiation temperature and alloying element. Several models about this phase transformation are summarized at the same time.
(4) The techniques of X-ray diffraction and positron annihilation provide a new picture for the description of the microstructural evolution with parameters such as domain size, microstrain, and S-parameter. Usually, with an increase in dose, the microstrain increases and the domain size decreases. The S-parameter also increases due to the ion irradiation.
(5) As complementary experiments, the annealing behavior of these irradiation defects is also studied. The <c>-dislocation loops grow to a large size and the Kr bubbles grow with the surface diffusion mechanism. For the recrystallization of $Zr(Fe,Cr,Nb)_2$ precipitates, it starts at 723–873 K and involves the rearrangement of alloying elements and the dissipation of vacancies to the matrix.
(6) The ion irradiation changes the mechanical and corrosion behaviors significantly. The dislocation loops and bubbles serve as obstacles for dislocation gliding, so hardness and activation energy in indentation creep increase due to irradiation. The alloy composition, texture, and grain shape have a great effect on the irradiation growth. For high temperature oxidation, the ion irradiation enhances the oxidation process. The electrochemical behavior is determined by the balance between irradiation damage and oxidation protection.

For the ion irradiation effect of zirconium alloys, it is not well understood. Understanding these mechanisms is useful for the development of new advanced materials tolerant of high irradiation doses. To the simulation of neutron radiation of zirconium, on one hand, more experimental research is needed to accumulate basic data about irradiation. On the other hand, some models could be established by the help of computer simulation. The ion irradiation of zirconium could indicate the relationship of microstructure-properties under irradiation to some extent. More importantly, the illustration of neutron irradiation mechanisms can be enhanced by the study of the ion irradiation research.

Conflict of interest

There are no conflicts of interest.

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