Chapter 6
Irradiation Behavior in Entropic Materials

As we all know, the irradiation can produce a wide variety of microstructural changes in metals and alloys, including the formation of point defects such as self-interstitial atoms and vacancies, defect clusters such as dislocation loops and stacking fault tetrahedrons, and cavities such as voids and the gas-filled bubbles. In a word, the effects of irradiation on the microstructural evolution of metals and alloys will induce the properties of nuclear materials degradation. This article overviews the effect of irradiation on the microstructure and mechanical properties in the candidate nuclear materials to improve our understanding of behaviors under irradiation, with an emphasis on the prospects of developing improved high-performance structural materials with high resistance to radiation-induced property degradation. It is also now beginning to provide guidance for the development of new alloys, such as entropic alloys.

6.1 Introduction

Since civilization began, the development of metallic alloys with better strength and more ductility have repeatedly changed human culture and capacity. Scientific breakthroughs are increasingly required to meet the extreme environments such as high-temperature and high-dose requirements. So far, the entropic alloys, consisting of two to five (or more) elements at high concentrations or near equiatomic composition such as the concentrated solid solution alloys and high-entropy alloys have attracted the increasing attention due to the fact that the selected alloys show the superior resistance to radiation swelling [1] and radiation damages by adjusting the elemental composition and the number of elements in the entropic alloys. Also, the entropic alloys can suffer so high radiation dose to about 100 dpa ions irradiation.

In addition, with the increasing of the performance of high-entropy alloys under irradiation, a lot of research work shows that high-entropy alloys have the sluggish diffusion effect due to the synergy between each other in every atom diffusion effect is restrained, preventing the atomic motion in the lattice site, depressing the effective diffusion rate of atoms in the alloys. Moreover, the existence of higher atomic-level

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stress gives it a self-healing mechanism [2, 3]. Accordingly, the high-entropy alloy has excellent irradiation resistance due to the particularity of structure, especially, the structure of chemical disorder and unique site-to-site lattice distortion in high-entropy alloys. So far, the high-entropy alloys have become a research hotspot in the field of nuclear structure materials. It is mainly seen in Zhang [4, 5] and Jin [6, 7] from Oak Ridge Laboratory in the United States, Lu [8, 9] from the University of Michigan, Nagase [2, 10, 11] and Egami [3] from Osaka University in Japan, and Xia and Zhang [1, 12] from Peking University and University of Science and Technology, Beijing.

The research on the radiation damage characteristics of high-entropy alloys are divided into the following aspects: Phase structure stability and microstructure evolution under irradiation such as the evolution of irradiation defects, radiation-induced precipitation, volume swelling rate, irradiation mechanism, and the relevant theoretical simulation.

6.1.1 Microstructural Evolution

According to thermodynamics knowledge of the Gibbs free energy with the equation $\Delta G_{mix} = \Delta H_{mix} - T\Delta S_{mix}$, the multicomponent high-entropy alloys will have lower Gibbs free energy at high temperatures, and the structure will be more stable. Senkov [13] have confirmed that the selected NbMoTaW and NbMoTaWV high-entropy alloys exhibit high phase structural stability at high temperatures. Besides, some selected high-entropy alloys, they also show high-phase structure stability under irradiation conditions. For example, Nagase [2] studied CoCrCuFeNi five-element FCC structure high-entropy alloy with the in situ electron irradiation. When the temperature was increased to 500 °C and the irradiation dose exceeded to 45 dpa, the phase structure stability still remained as there was no any grain coarsening. To this end, the author believes that the atomic diffusion mechanism of high-entropy alloys under the irradiated environment is different from that of heat treatment. Figure 6.1 shows the transmission electron microscopy (TEM) images of CoCrCuFeNi high-entropy alloy at different irradiation doses at different temperatures [2]. It is worth noting that under such high-temperature irradiation conditions, the TEM image is indistinct due to the presence of heat flow. In addition, the multicomponent alloy ZrHfNb with BCC structure has a high-phase structure stability at room temperature with an electron irradiation dose of ~10 dpa.

Comparing with the phase stability of other materials under irradiation conditions, such as Zr-based [14] and Cu-based bulk amorphous alloys [15], can be found in the nanocrystalline structures under the irradiation condition. The main reason is attributed to the occurrence of stress fluctuation under irradiation conditions, resulting in a decrease in the stability of the amorphous phase structure, resulting in precipitation of nanocrystals. However, there is no certain conclusion for the reason that amorphous alloys are crystallized by ion irradiation. Xia and Zhang studied the phase structure stability of $Al_{1.5}$CoCrFeNi high-entropy alloy with two-phase struc-

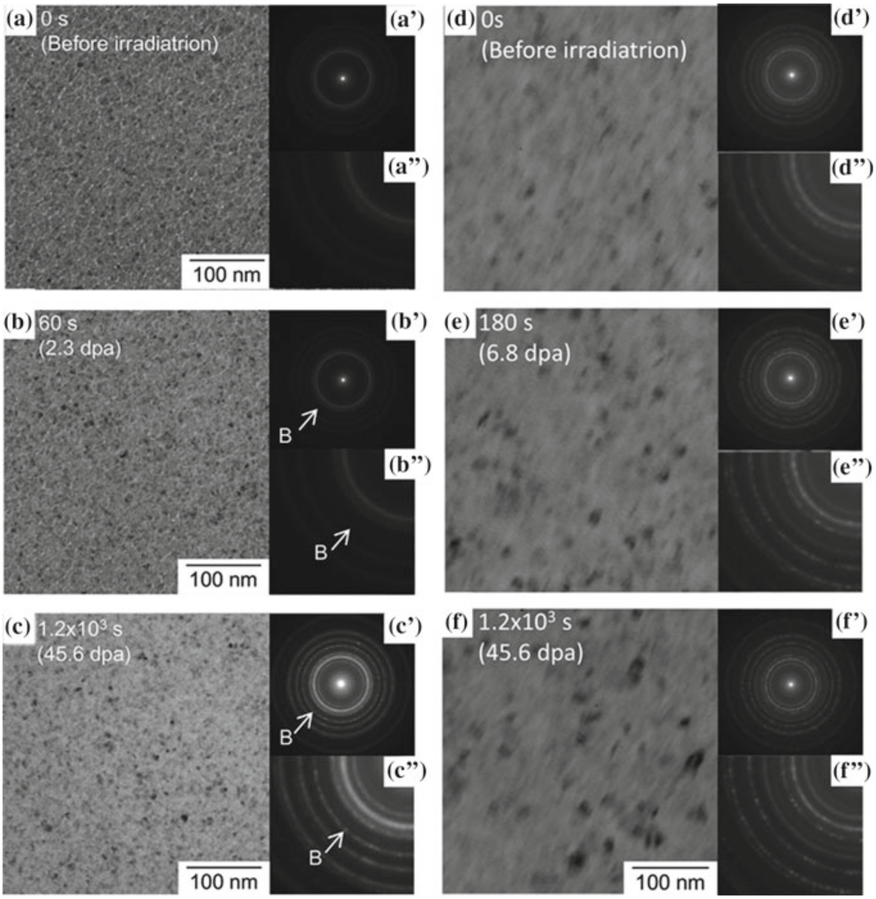

Fig. 6.1 In situ transmission electron microscopy image of CoCrCuFeNi high-entropy alloy under different irradiation conditions [2], **a**–**c** normal temperature; **d**–**f** 500 °C

ture before and after Au^+ ion irradiation at room temperature. It was found that the irradiation dose was ~50 dpa, and the matrix phase and the precipitate phase did not significantly dissolve. After ion irradiation, the alloy exhibits high-phase structure stability [1]. The transmission electron microscopy image of $Al_{1.5}CoCrFeNi$ before and after normal temperature ion irradiation is shown in Fig. 6.2.

Under the ion irradiation experiment, for the Ni-containing single-phase FCC multicomponent alloys, ORNL researchers found that the defect size of NiCo and NiFe binary alloy is lower than that of pure Ni under Au^+ ion irradiation, but the defect density is higher [5], as shown in Fig. 6.3.

In addition, Lu [9] also carried out the similar research on Ni-containing multicomponent single-phase FCC structural alloys, and found that with increasing the number of components in the Ni-containing multicomponent alloys, the depth where

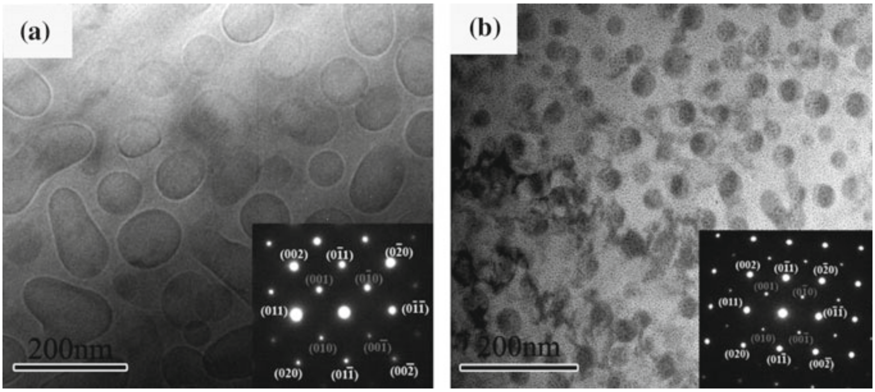

Fig. 6.2 BF-TEM image and SAED of $Al_{1.5}CoCrFeNi$ alloy before and after irradiation [1], **a** before irradiation; **b** after irradiation 3 meV Au^+, ~50 dpa

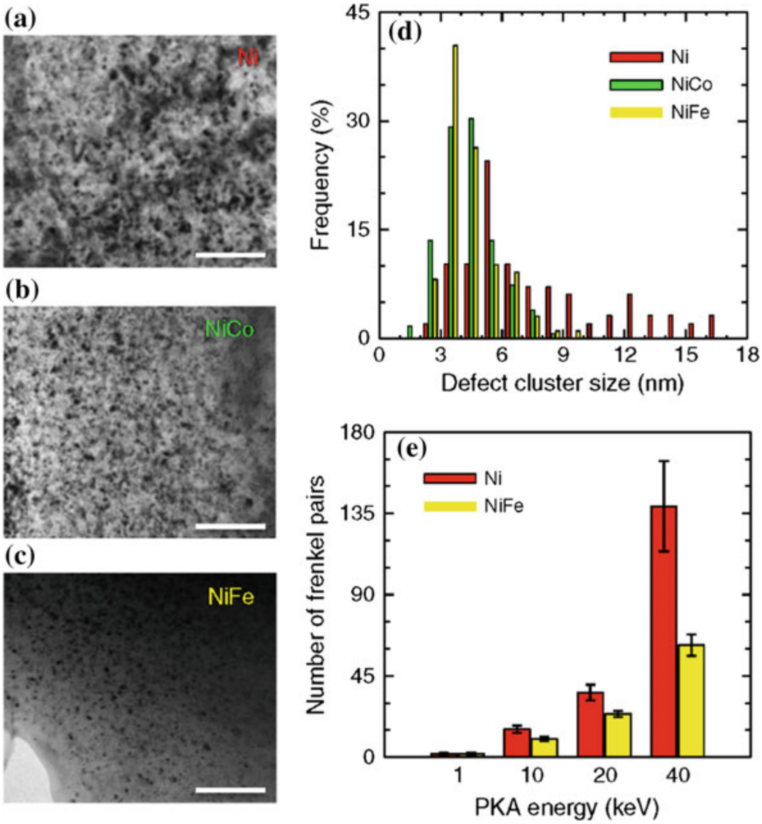

Fig. 6.3 Distribution of defect size of NiCo and NiFe binary alloys and pure Ni under ion irradiation conditions [5]

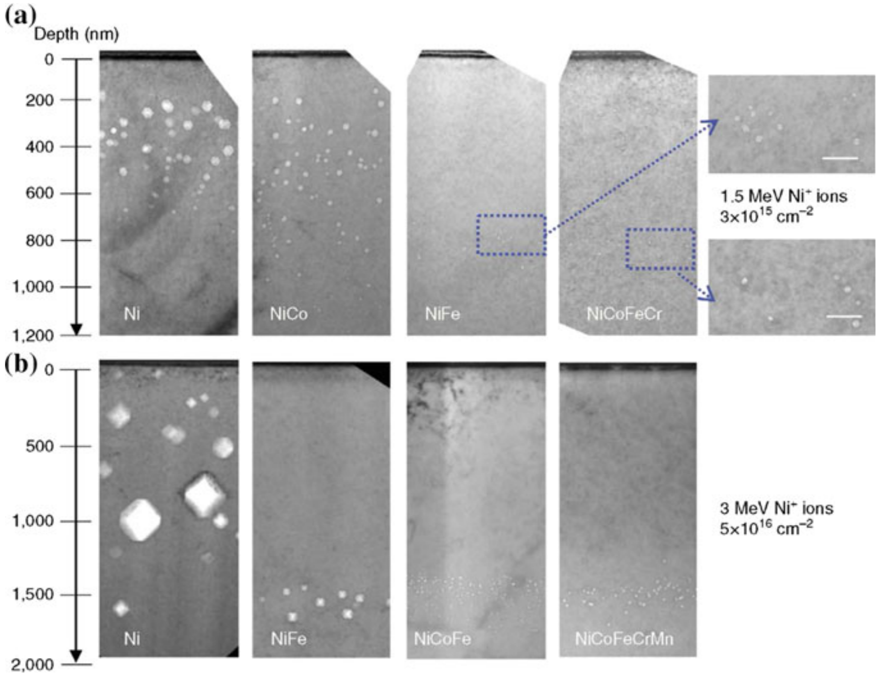

Fig. 6.4 The distribution of voids in pure Ni and Ni multicomponent alloy under irradiation conditions [9]

the voids form is deeper while the size of the voids is smaller, as shown in Fig. 6.4. The reason for this phenomenon is that as the number of components increases, the probability of recombination of the irradiation-induced point defects increases, suppressing a large number of vacancies are formed to form larger sized voids.

In addition, Kumar [16] compared the density distribution of dislocation in CrFeNiMn quaternary high-entropy alloy and austenitic stainless steel at different irradiation temperatures. It is found that the density of dislocation loops in CrFeNiMn high-entropy alloy decreases linearly with increasing the irradiation temperature. At 700 °C, the density of the dislocation loop in the high-entropy alloy is about 100 times than that of an austenitic stainless steel. It should be noted that the average size of the dislocation loops in the austenitic stainless steel is much higher than that of FeCrNiMn under high-temperature irradiation conditions. Through the results of in situ electron irradiation, He et al. reported that the CoCrFeNi high-entropy alloy increases with the increase of irradiation metering, and the dislocation loop size increases much faster than pure Ni [17].

Generally speaking, high-entropy alloys maintain high-phase structural stability during electron or ion irradiation experiments. For Ni-containing multicomponent alloys, the radiation defects of multicomponent alloys are smaller than ordinary metals or alloys in terms of radiation defect evolution, while the dislocation density is large. In addition, with the increase of the number of components, the probability of short-distance recombination of multicomponent alloy irradiation defects increases, which can effectively avoid the formation of voids by a large number of vacancies based on the previous report.

6.1.2 Segregation

Under irradiation conditions, the redistribution of the solute atoms leads to segregation of atoms during irradiation, leading to precipitation. He [18] studied the segregation of solute atoms in CoCrFeNi, CoCrFeMnNi, and CoCrFeNiPd under the electron irradiation dose of ~1 dpa at 400 °C. It is found that CoCrFeNi exhibits high-phase structure stability, while CoCrFeNiMn has a sequence phase $L1_0$ (NiMn)-ordered phase precipitation, and CoCrFeNiPd has a metastable decomposition between Co/Ni and Pd [18].

For the segregation behavior of solute atoms under irradiation conditions, in general, smaller solute atoms tend to concentrate at the dislocation loop, while positive enthalpy makes the atoms tend to segregate. The atomic size difference and the mixed enthalpy compete with each other, resulting in different precipitation behaviors of the three alloys. In the CoCrFeNi high-entropy alloy, Co/Ni atoms are enriched in the gap dislocation loop. However, due to the effect of mixed enthalpy, Co and Ni are easily segregated at the dislocation loop from the atomic radius, but due to Ni and Mn have a negative mixed enthalpy. At this time, the effect of elemental mixing enthalpy is greater than the influence of atomic radius difference, so the addition of Mn element affects the segregation of Ni element, resulting in the ordered phase $L1_0$ (NiMn) in CoCrFeNiMn high-entropy alloy. Similarly, the metastable decomposition between Co/Ni and Pd occurs in the CoCrFeNiPd high-entropy alloy due to the action of mixed ruthenium. For this reason, both the mixed enthalpy and the atomic radius difference have an important influence on the segregation behavior of the solute atoms of the high-entropy alloy under irradiation conditions. In addition to that, there may be other factors that further influence the radiation precipitation behavior. However, it has been shown that the precipitation of ordered phases of high-entropy alloys under irradiation conditions may promote the improvement of the anti-irradiation properties of high-entropy alloys to some extent reported by Koch [19].

6.2 Volume Swelling

When the material is under heavy ion irradiation conditions, the damage causes the volume swelling. Jin et al. [6] studied the variation of the volume swelling rate of multicomponent alloys with the increase of the number of components under ion irradiation conditions. It was found that the volume swelling rate is reduced with increasing the number of components in multicomponent alloys, and the volume

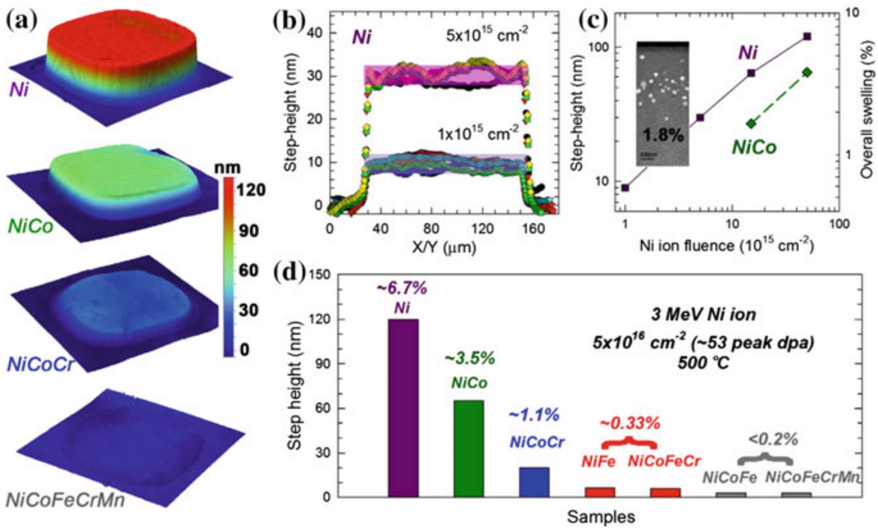

Fig. 6.5 Comparison of the volume swelling ratio of multicomponent alloys with the number of components **a** three-dimensional view of radiation swelling; **b**–**d** comparison of step heights between irradiated and nonirradiated areas of multicomponent alloy [6]

swelling rate is Ni > FeNi ≥ CoCrFeNi > CoFeNi ≥ CoCrFeMnNi, as shown in Fig. 6.5. This further reveals that entropy has a certain effect on multicomponent alloy anti-ion irradiation, but it is also affected by other factors, resulting in binary alloy and quaternary alloy with considerable volume swelling rate, showing nonlinearity relationship.

6.3 Mechanical Properties

The compressive stress–strain curve of the metallic material under irradiation conditions has a serration and flow unit phenomenon. While, so far, there is no any stress–strain curves for high-entropy alloys under in situ irradiation conditions. The so-called serration behaviors in the stress–strain curve actually refer to a change failure of materials. The earliest deformation is accompanied by the emission of noise. Accordingly, the "tin cry" sound can be heard. Also, for the "tin cry", the dislocation deformation mechanism, namely twinning deformation mechanism will be occurring.

Recently, in the study of high-entropy alloys under extremely low-temperature or high-speed loading conditions or high-temperature deformation, a unique serration behavior has been discovered. Especially, when the single-crystal copper was subjected to compression test in situ irradiation environment, an obvious serration behavior was found on the compressive stress–strain curve, as shown in Fig. 6.6. The

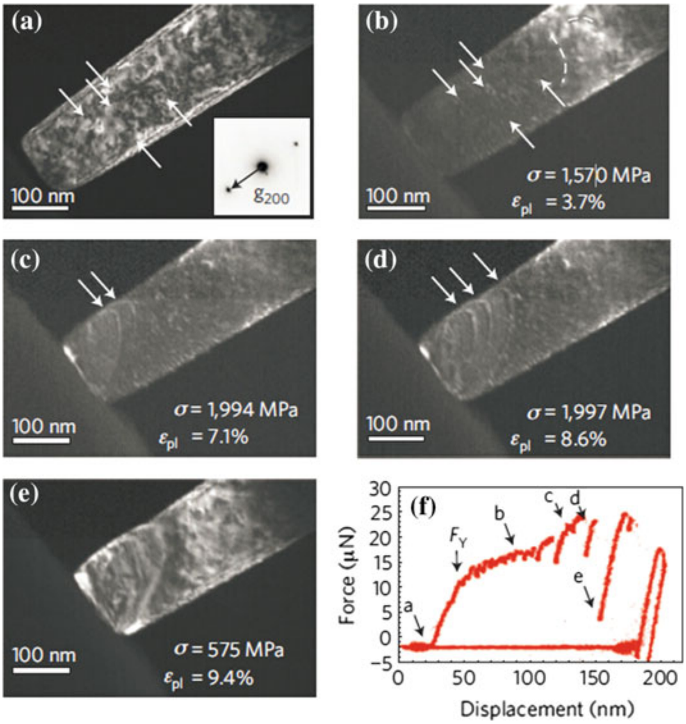

Fig. 6.6 The serration phenomenon of single crystal copper under the in situ irradiation environment of nanoscale based on in situ observation [20], **a**–**e** In situ compression images at different time points; **f** the compression stress–strain curves

emergence of this phenomenon has a certain revealing effect for further explaining the causes of serration and flow unit. Because of the atomic migration inside the material, there are many point defects in the irradiation environment, showing that the whole serration is inseparable from the movement under the specific conditions of dislocation.

At present, the research on the mechanical properties of high-entropy alloys under irradiation conditions is mainly related to the performance test of nanoindentation. Figure 6.7 shows the ratio of hardness to unirradiated hardness of CrFeMnNi quaternary high-entropy alloy after irradiation under different irradiation conditions. It can be found that: (1) at the same irradiation temperature, the hardness of the alloy increases with the increase of the irradiation dose; (2) at the same irradiation dose, the temperature rises, and the radiation hardening of the alloy is weakened.

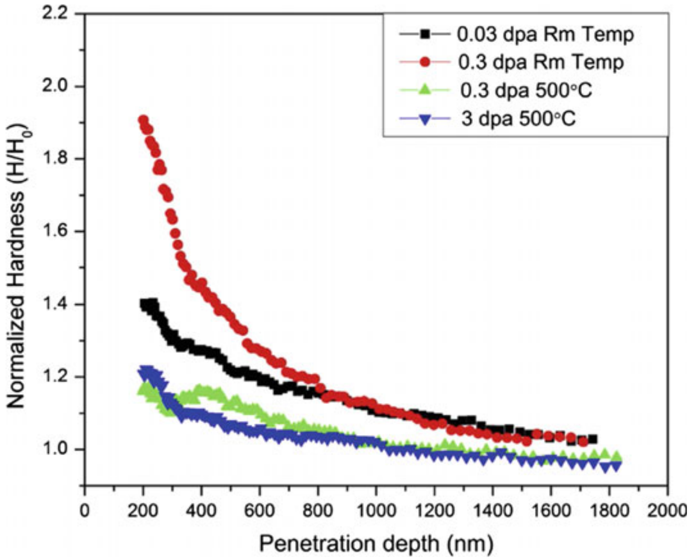

Fig. 6.7 The ratio of CrFeMnNi high-entropy alloy after irradiation and non-irradiation hardness under different irradiation conditions [16]

6.4 Modelling

The theoretical simulation of multicomponent alloys is mainly to explain the movement of defects in high-entropy alloys under irradiation conditions. Zhao [21] calculated the diffusion mechanism of interstitial atoms in Ni, NiFe, NiCo, and CoCrNi using the first-principles molecular dynamics method of density functional theory (DFT). The results show that the diffusion of interstitial atoms in multicomponent alloys has a quite lower diffusion, which can effectively explain the atomic segregation of high-entropy alloys under irradiation conditions and the phase structure transformation caused by atomic segregation [22]. Zarkadoula [22] applied the similar molecular dynamics combined with the dual temperature model method to study the evolution of the off-grid collision and defect structure of Ni and NiFe in FCC structure under irradiation environment. It is found that the number of self-gap atoms and vacancy defects in Ni and NiFe reaches a maximum in the initial very short time of the cascade collision, and then recombines from the interstitial atoms and vacancy defects and rapidly decreases in 1 ps. There are a small number of Frankel defects present. Comparing the number of Frankel defect pairs after 1 ps in Ni and NiFe, it was found that the Frankel defect pair in NiFe is less than Ni, as shown in Fig. 6.8. At the same time, it is found that the electron temperature of NiFe is higher than that of Ni in the cascade collision process, which means that it can greatly promote the recombination of point defects in NiFe.

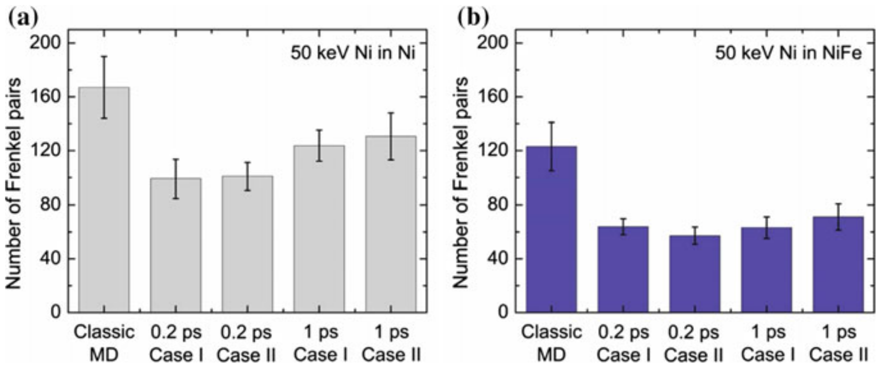

Fig. 6.8 Comparison of the number of Frankel defect pairs of Ni and NiFe at 0.2 ps and 1 ps, respectively, in PKA cascade collision [22]

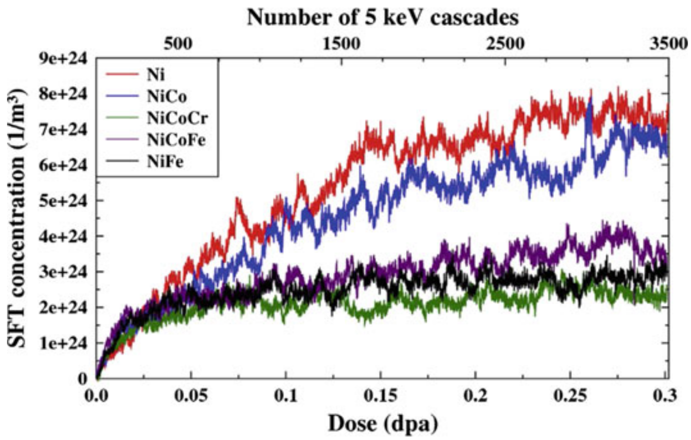

Fig. 6.9 Dependence of stacking tetrahedral concentration and irradiation dose in Ni multicomponent alloys [23]

In addition to that, another author Levo [23] compared the density of irradiation defects at different irradiation doses in pure Ni and Ni multicomponent alloys, showing that CoCrNi can reach equilibrium at a small irradiation dose. It means that in the initial stage of cascade collision, the multicomponent alloy can be quickly quenched and annihilated between the irradiation defects, thus achieving the balance of point defects, as shown in Fig. 6.9.

6.5 Irradiation Mechanism

(1) Self-healing mechanism

Egami [3] indicate that the multicomponent alloys have certain atomic-level stresses due to the difference in atomic size by simulations, i.e., the atomic-level stress promotes the local amorphization of the alloy under the irradiation conditions. Meanwhile, it will accumulate a large amount of thermal energy, which is sufficient to locally melt and recrystallize the multielement alloy, inducing the multielement alloy to have a lower dislocation density. It is further noted that the multicomponent alloy has a good "self-healing" ability when the atomic-level volume strain is close to 0.1. Figure 6.10 shows the schematic illustrations of the simplest type of defects introduced by the electron knock-on effect under MeV electron irradiation, and the defect recovery processes in single-element solid solutions as a typical example of conventional metallic materials and high-entropy alloys. It can be concluded that the high atomic-level stress in HEAs may facilitate amorphization upon irradiation, followed by recrystallization. Hence, this process is expected to leave much less defects in HEAs than in conventional materials.

In general, the "self-healing" mechanism of high-entropy alloys under irradiation conditions is only an explanation for the irradiation resistance performance of high-entropy alloys. As for the further revealing of the irradiation mechanism, many detailed and systematic methods are still needed.

(2) Reduction in electron mean free path

Zhang from the ORNL reported that for the concentrated solid solution alloys, increasing the number of elements or adding/altering some specific elements can lead to a substantial reduction in electron mean free path and orders of magnitude decrease in electrical and thermal conductivity using KKR-CPA method. Consequentially, the suppressed damage accumulation with increasing chemical disorder from pure nickel to binary and to more complex quaternary solid solutions is observed. Lu also reported that a higher fraction of dislocation loops exist in the more compositionally complex alloys, which indicate that increasing compositional complexity can extend the incubation period and delay the loop growth. The main reason is that the short-range motion of interstitial clusters in high-entropy alloys significantly increases the vacancy-interstitial recombination rate plays a key role in preventing significant void swelling in concentrated solid solution alloys, such as the NiFe, NiCoFe, NiCoFeCr, and NiCoFeCrMn alloys. And, the mechanism has been revealed by TEM observation and confirmed by MD simulation. The MD simulation was shown in Fig. 6.11.

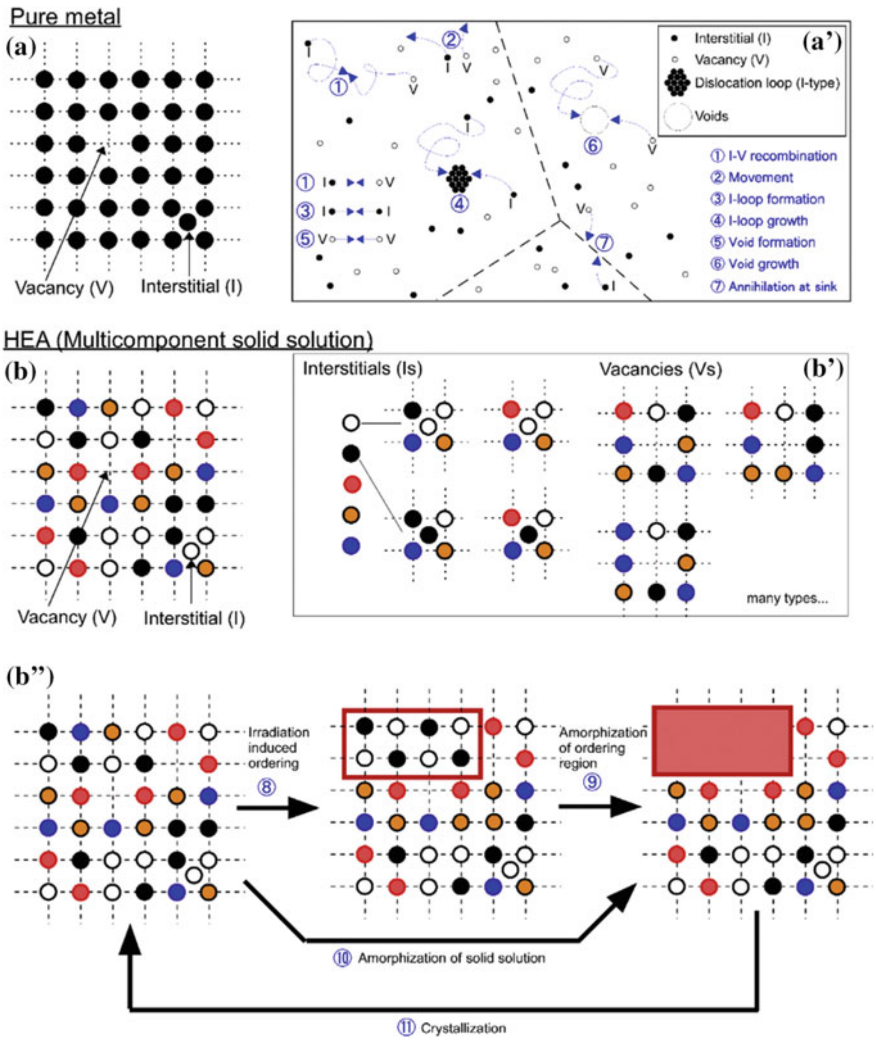

Fig. 6.10 Schematic illustration of the self-healing mechanism under MeV electron irradiation [2]

6.6 Conclusion

In summary, lots of experimental studies and simulations were conducted on the irradiation behavior in high-entropy alloys. Due to the special structure of the entropy alloys, the alloys have high structural stability of high-temperature phase and excellent radiation resistance, whether it is the nuclear fuel cladding material in the fission reactor or the first wall material in the fusion reactor. The development of advanced Generation IV fission reactor and fusion energy systems are directly linked to the

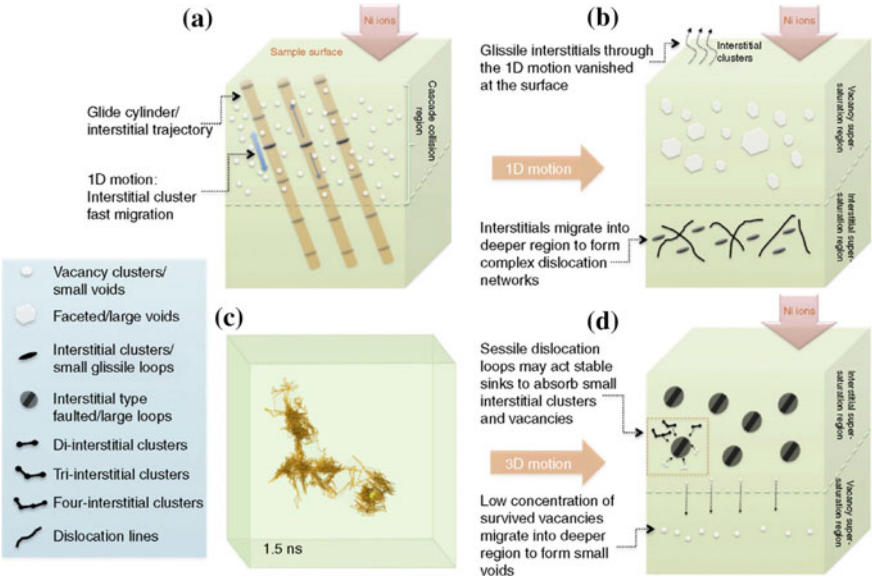

Fig. 6.11 1D and 3D motions of interstitial clusters under ion irradiation [9]

materials challenges associated with the higher radiation dose and higher temperatures. The materials research challenges that need to be successfully resolved for fission and fusion energy systems might be successful due to the more elements and high concentrations of elements in the materials, such as entropic alloys.

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