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Irradiation Behavior in High Entropy Alloys

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Abstract: As an increasing demand of advanced nuclear fission reactors and fusion facilities, the key requirements for the materials used in advanced nuclear systems should encompass superior high temperature property, good behavior in corrosive environment, and high irradiation resistance, etc. Recently, it was found that some selected high entropy alloys (HEAs) possess excellent mechanical properties at high temperature, high corrosion resistance, and no grain coarsening and self-healing ability under irradiation, especially, the exceptional structural stability and lower irradiation-induced volume swelling, compared with other conventional materials. Thus, HEAs have been considered as the potential nuclear materials used for future fission or fusion reactors, which are designed to operate at higher temperatures and higher radiation doses up to several hundreds of displacement per atom (dpa). An insight into the irradiation behavior of HEAs was given, including fundamental researches to investigate the irradiation-induced phase crystal structure change and volume swelling in HEAs. In summary, a brief overview of the irradiation behavior in HEAs was made and the irradiation-induced structural change in HEAs may be relatively insensitive because of their special structures.

Key words: high entropy alloy; irradiation behavior; self-healing; structure change; volume swelling

The rapidly growing energy demand and more considerations in environmental issues impel nuclear energy to play an important role among other energies. Currently, about 430 commercial nuclear power reactors in the world provide about 11% of the world's supply of electricity. A vast majority of structural materials are playing important roles in fission reactors. To improve the safety and efficiency of nuclear reactors, the development of novel and advanced nuclear structural materials with high resistance to irradiation damage is necessary. In many cases, a key strategy for designing high resistance to irradiation damage materials is based on high temperature phase stability, high temperature strength, and dimensional stability under irradiation conditions, because irradiation can result in the increase of defect densities, which impedes dislocation motion and increases flow stress. During plastic loading, a vast majority of dislocation glide can cause the absorption of defects, leading to strain softening and yield drop. In addition, the interaction between solute atoms and point defects can cause coupled transport of solute atoms by point defect fluxes[1], giving rise to solute segregation phenomena and leading to void swelling and structural changes. The structural materials for advanced nuclear systems need to endure much higher neutron doses, higher temperatures and extremely corrosive environment, which are beyond the performances of materials used in current nuclear systems. In general, conventional materials for nuclear reactors include various ferritic/martensitic steels[2], austenitic stainless steels[3], zirconium alloys[4-6], ceramics, and composites, etc. They might have a limit to endure the high irradiation dose and the severe environment in future nuclear system.

In order to endure the irradiation threats to the operation of structural materials used in nuclear systems, novel structures, which possess high irradiation resistance, should be developed. Recently, high entropy alloys (HEAs)[7-12], also termed multi-base alloys (MBAs), are being developed. As equi-atomic or approximately atomic, multi-element metallic systems, the MBAs generally have at least 3 major metallic elements with high concentrations (5 at.% to 35 at.%), and the multiple elements with different crystal structures can crystallize as a relatively simple phase, because the configurational

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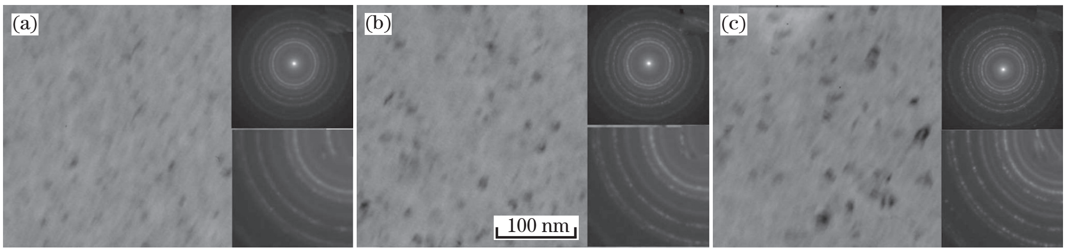
entropy has the contribution to the total free energy in alloys. High entropy may stabilize the disordered solid-solution state rather than multi-phase microstructures, which distinguishes HEAs from conventional alloys, and the mixing of various elements leads to the possibility of high irradiation resistances via the unique “self-healing” mechanisms[13]. In contrast to conventional alloy systems, HEAs tend to form a simple solid solution structure, such as face-centered cubic (FCC), body-centered cubic (BCC), or a mixture of both, which is due to the high entropy of mixing of the solution phases[14]. Recent results in HEAs are presented to demonstrate how atomic-scale characteristics can provide a high irradiation resistance. In this article, the irradiation behavior of HEAs with high phase stability under fast electron or accelerated MeV heavy ion irradiations was reviewed. Different structures of HEAs were described in more detail with an emphasis on the irradiation behavior of recent correlative researches. Besides, the “self-healing” process in HEAs was proposed.

1 Phase Stability of HEAs against Irradiation

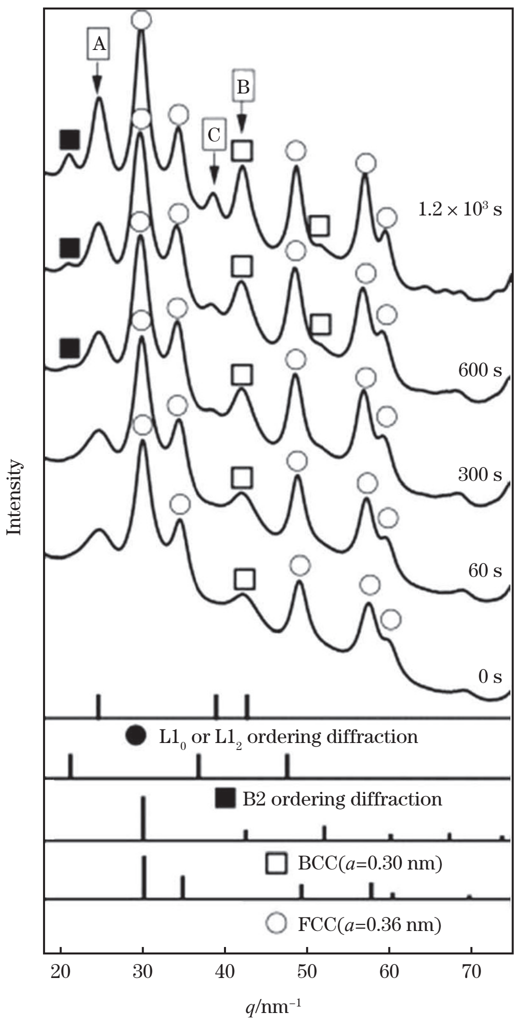
The structural changes in an FCC CoCrCuFeNi high entropy alloy obtained by sputtering (thickness: 25 nm, 100 nm and 1 μm) under MeV electron irradiation were investigated with a high voltage electron microscope (HVEM)[15]. The results confirmed that the FCC solid solution exhibited high phase stability against irradiation, and the FCC phase remained as the main constituent phase over 40 dpa (displacement per atom) of irradiation at 298 K and 773 K, respectively. Moreover, although the irradiation produced in this alloy was similar to the structural changes induced by thermal annealing, the irradiation-induced grain coarsening did not occur at 773 K as well as at 298 K. Fig. 1 shows the in-situ transmission electron microscopy (TEM) images of structural changes in a 100 nm thick specimen of CoCrCuFeNi HEA irradiated by MeV electron at 773 K[15]. The grain coarsening caused by irradiation could not be seen in bright field (BF) images (Figs. 1(a)−1(c)) at 773 K, and the corresponding selected-area diffraction (SAD) patterns indicated the irradiation-induced structural changes. The number and the position of Debye rings in SAD patterns tended to increase with increasing the irradiation dose. To understand the irradiation-induced changes observed in SAD patterns, the electron diffraction intensity profile was analyzed and the results are shown in Fig. 2[15]. Before irradiation, the main constituent phase was identified as the FCC phase accompanied with a minor phase of BCC solid solution; the BCC phase increased with increasing irradiation time, but the FCC phase remained as the main constituent phase. Similarly, another different structure HEA, BCC solid solution Zr-Hf-Nb[16-18], did not exhibit any obvious structural change after about 10 dpa irradiation at 298 K, revealing a high phase stability against irradiation damage.



(a) Before irradiation; (b) After irradiation for 180 s, 6.8 dpa; (c) After irradiation for 1.2×10^3 s, 45.6 dpa.

Fig. 1 In-situ TEM images showing the changes in the structure of a 100 nm thick specimen of CoCrCuFeNi HEAs irradiated by MeV electron at 773 K

The present authors prepared a five-element high entropy alloy, Al_xCoCrFeNi (x = 0.1, 0.75, and 1.5 in molar ratio, for simplicity, they are denoted by Al0.1, Al0.75 and Al1.5, respectively) by vacuum levitation melting (VLM) with varying Al contents, which can form different structures[19]. Then, the $Al_{1.5}$CoCrFeNi HEA with BCC structure was further studied by TEM. The TEM micrographs of the $Al_{1.5}$CoCrFeNi alloy sample before and after Au-ion irradiation were compared and are shown in Fig. 3[20]. The insets in the TEM micrographs, as shown in Figs. 3(a) and 3(b), are the corresponding SAD patterns. It showed that after irradiation, the sample structure did not change. The TEM image also indicated that there was no obvious mixing between the matrix and particle under irradiation. However, numerous black spots could be observed in Fig. 3(b), which may be caused by the irradiation-induced element segregation. Moreover, the authors' research also verified that the value of void swelling in $Al_{1.5}$CoCrFeNi alloy was quite lower than those of other typical nuclear alloys under similar irradiation conditions[20]. In contrast, in some amorphous alloys or bulk metallic glasses (BMGs), such as Zr-based binary BMGs[21], electron irradiation could lead to the formation of nano-crystalline. It indicated that the amorphous phase in Zr-based binary BMGs was not stable under electron irradiation, but the crystalline phase which required to resist electron irradiation might be stable. In addition, in nano-structured Cu-based alloys, such as $Cu_{93.5}W_{6.5}$ and



The peaks indicated by A, B and C appeared after irradiation.

Fig. 2 Changes in electron diffraction intensity profile of a 100 nm thick specimen of CoCrCuFeNi HEAs under MeV electron irradiation at 773 K

$Cu_{99}W_1$, W-containing nano-precipitates also formed under irradiation to resist irradiation[22,23]. In addition, in previous research[20], it was found that the irradiation-induced volume swellings in Al_xCoCrFeNi HEAs were lower than those of conventional nuclear materials under similar irradiation, and the order of volume swelling in alloys was: FCC< FCC + BCC < BCC, while the order is BCC < FCC for conventional materials[24]; all alloys showed exceptional structural stability when irradiated not lower than 50 dpa at 298 K.

In a word, the irradiation responses in HEAs, amorphous and nano-structured alloys are distinctly different. Amorphous alloys are not stable until some nano-precipitates appear under irradiation, similar to nano-structured Cu-based alloys.

2 Mechanical Properties after Irradiation

The mechanical properties including nano-hardness and modulus of the Al_xCoCrFeNi HEAs under heavy Au-ions irradiation were investigated by using nano-indentation. Fig. 4 displays corresponding typical load-displacement curves for virginal and as-irradiated alloys with different compositions and structures. The structure of $Al_{0.1}$CoCrFeNi, $Al_{0.75}$CoCrFeNi, and $Al_{1.5}$CoCrFeNi is FCC, mixing of FCC and BCC, and BCC, respectively. As shown in Fig. 4, the nano-hardness and modulus of the irradiated alloys increased gently with increasing Al content. Table 1 shows the average value of nano-hardness and modulus for virginal and irradiated alloy. Each data listed in Table 1 represents the average value of five indentation measurements. The nano-hardness was calculated by the method of Doerner[25] for the interpretation of data from nano-indentation instruments, using the equation:

$$H = \frac{P}{A} \tag{1}$$

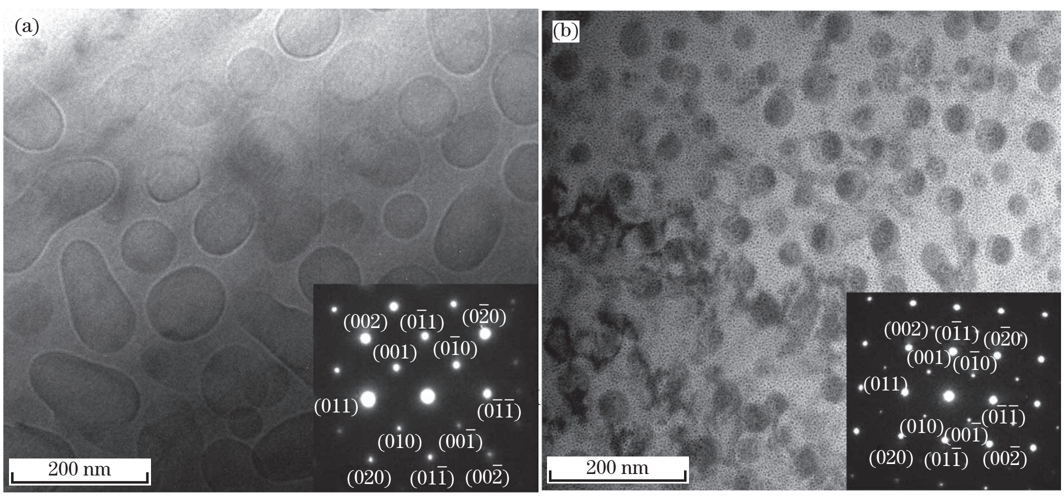


Fig. 3 TEM bright field image of $Al_{1.5}$CoCrFeNi HEA before (a) and after (b) Au-ion irradiation of 3 MeV Au ions at 1×10^{16} cm^{-2}

where, P is the maximum load; and A is the projected area of the indentation. The calculation of modulus was based on the obtained stiffness (S) data, which represents the resistance of a material to elastic deformation:

$$S = \frac{dP}{dH} \quad (2)$$

where, dP is the load variation; and dH is the related displacement. Again, modulus E is calculated by Eq.(3).

$$E = S\sqrt{\pi}/2\beta\sqrt{A} \quad (3)$$

where, the value of β is based on the indenter geometry and S is obtained from Eq. (2). The increase in the hardness of alloy is due to the irradiation-induced defects, which cause the pinning of shear bands. The improvement in the elastic modulus may be due to the nano-structured precipitates, which requires further confirmation.

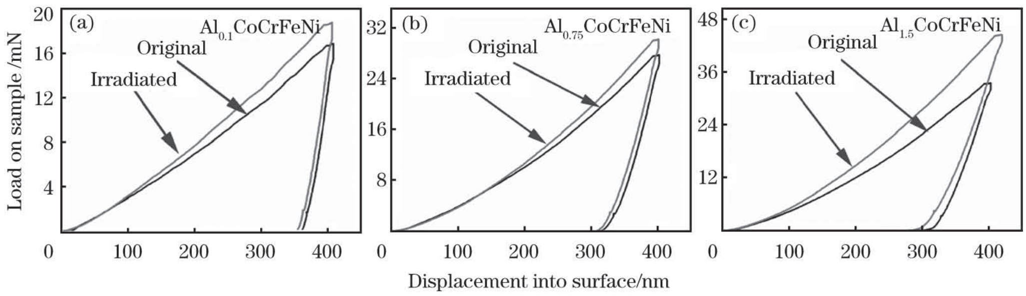


Fig. 4 Displacement *vs.* force curves for virginal and irradiated HEAs

Table 1 Average value of nano-hardness and modulus for virginal and irradiated samples GPa

Composition	Condition	Average modulus	Average hardness
Al0.1	Virginal	380.8	11.11
	Irradiated	390.7	13.17
Al0.75	Virginal	406.4	19.36
	Irradiated	412.4	19.47
Al1.5	Virginal	465.8	27.01
	Irradiated	472.3	29.35

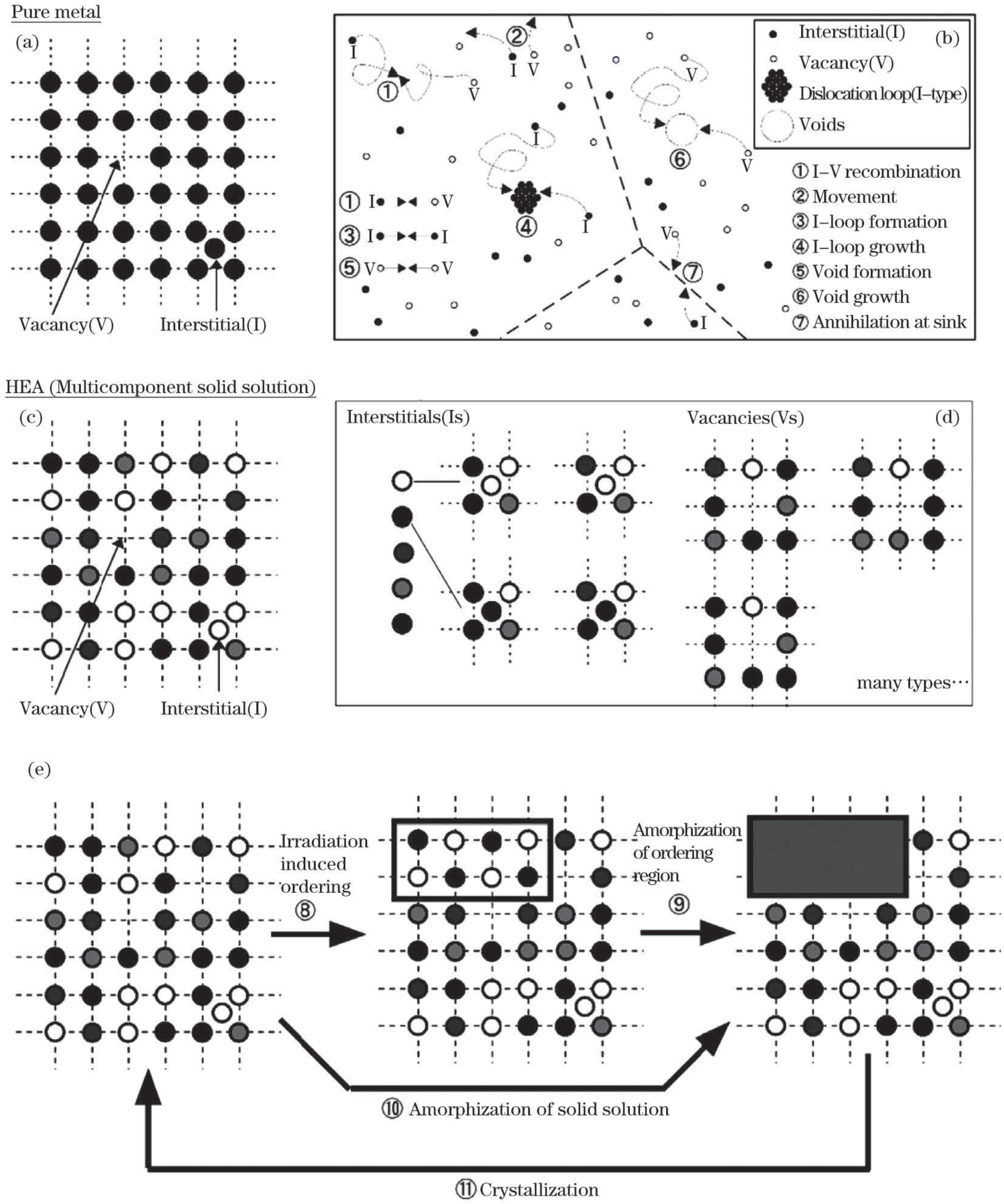
3 "Self-healing" Process in HEAs

Under irradiation of energetic particles, point defects including interstitial and vacancy, formed through atoms displacement by the ion[26,27], electron[15-18] or neutron[28] collisions. Generally, the number of interstitial and vacancy formed by any form of irradiation is equal. The schematic illustration of single component crystal and HEAs for the evolution of interstitial and vacancy is presented in Fig. 5[15]. In the single component crystal (Fig. 5(a)), the type of interstitials and vacancies is less than that in the high entropy alloys, and a vast majority of interstitials and vacancies can cause lots of dislocation loops including interstitial and vacancy types. Under irradiation, lots of vacancies gathered to cumulate voids leading to irradiation-induced volume swelling (Fig. 5(b)). On the contrary, in the case of HEAs under irradiation, as illustrated in Fig. 5(d), various types of interstitials and vacancies can form in HEAs because of the multiplicity of metallic elements. Various types of point defects in HEAs with equi-atomic or approximately compositions, which are different to those in conventional materials, maybe impliy shorter defect lifetime. Egami et al.[29] regarded the process as the "self-healing" process.

As shown in Fig. 5(d), many types of atomic vacancies and interstitials formed in HEAs under irradiation, exhibiting extremely high formation energy and high atomic-level stress[13] as well as low migration energy; thus, these types of vacancies and interstitials are unstable, and the high atomic-level stress may promote amorphization of HEAs upon irradiation (Fig. 5(e)), followed by recrystallization, resulting in the high recombination rate for the annihilation of these defects in order to decrease the strain. The process is expected to leave much less defects in HEAs than conventional materials, most likely, effective for restraining the formation of dislocation loops and voids. Thus, it can also be considered that the "self-healing" is accomplished via amorphization to crystallization process. The process of amorphization to crystallization occurred in some binary and ternary alloy systems[30].

4 Conclusions

Most issues on irradiation behavior in HEAs have been described. The "self-healing" process results in higher phase stability of HEAs against irradiation, compared with other materials, such as amorphous alloys and nano-structured alloys. In the amorphous and nano-structured alloys, irradiation in general leads to the formation of nano-precipitates. Both FCC, BCC and their mixing solid solution in high entropy alloys show high phase stability against irradiation damage, and the irradiation-induced volume swellings in Al_xCoCrFeNi HEAs are lower than those in conventional nuclear materials under similar irradiation. All alloys showed exceptional structural stability when irradiated over 50 dpa at 298 K.



(a), (b) Single component crystal; (c), (d), (e) HEAs.

Fig. 5 Schematic illustration of "self-healing" in HEAs

Furthermore, the modeling work is essential in developing high temperature stability, and high irradiation resistant structural materials suit for future nuclear reactor systems. Up to now, high entropy alloys with high irradiation resistance have proven to be one candidate material for innovative nuclear reactor systems. Finally, besides the experimental testing, a strong emphasis should be required to get full quantitative information on irradiation damage and carry out some modeling study. In addition, the equivalence among electron irradiation, ion irradiation and neutron irradiation and modeling study also needed for further research.

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