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Does the pathway for development of next generation nuclear materials straightly go through high-entropy materials?

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ABSTRACT

The concept of entropy stabilized complex materials provides a novel direction for the design and engineering of breakthrough materials to be used in extreme environments and particularly in advanced nuclear reactors. While still in its infancy, the use of high entropy materials (HEMs) in nuclear fusion/fission reactors is extremely promising. This mini review first gives a brief introduction to advanced nuclear reactors and their material requirements. Next, it summarizes recent advances in irradiation behaviors of high entropy alloys (HEAs). Additionally, challenges and perspectives regarding the irradiation behavior of HEAs and potential research directions are deduced.

1. Introduction

Nuclear power is a main component of the complex energy mixture and a key player in our transition from fossil fuels to carbon-free and safe energy supplies. However, the intrinsic drawbacks of nuclear power, such as long-lived radioactive waste, cost and safety, have held back widespread application of generation II and III (Gen II, III) fission reactors [1]. To address these concerns, advanced fission nuclear reactor concepts (generation IV, Gen IV) have been rigorously pursued. The most promising Gen IV systems include the sodium fast reactor (SFR), molten salt reactor (MSR), lead fast reactor (LFR) and the high temperature gas reactor (HTGR) [2]. All these Gen IV fission reactors can minimize nuclear waste, and increase capacity, efficiency, safety and sustainability to highly reduce cost and fuel usage [1,3]. However, in all these Gen IV fission systems, structural materials will be exposed to more aggressive environments. Moreover, while almost all current reactors are cooled with water, Gen IV reactors will use a wide range of liquid and gas coolants, which may be highly corrosive.

In contrast to nuclear fission, nuclear fusion is almost inherently safe and minimizes the generation of long-lived radioactive waste, which makes it a promising prospect for the large-scale generation of carbon-free energy. Similar to fission neutrons, the emitted fusion neutrons gradually diffuse into the reactor components surrounding the plasma, and subsequently create heat and displacement defects in the reactor materials through losing their energy. In addition to neutron bombardment, plasma-facing structural materials experience extreme heat loads, with temperatures in the range from 500 °C to more than 1000 °C [4]. These harsh conditions increase the risk of high temperature helium embrittlement in structural materials. Therefore, to support the undergoing plasma physics and reactor engineering challenges, the develop of novel materials with optimized properties is essential.

The concept of entropy stabilized multi-component alloys has opened the door to a wide range of possible compositions to design new materials with tailorable properties for a multitude of applications [5,6]. A particularly interesting application for these namely high entropy materials (HEMs) is in nuclear reactors. The virtually infinite compositional space of HEMs coupled with their particular characteristics, including high entropy, sluggish diffusion, lattice distortion, and cocktail effects, provide unlimited new opportunities to design and engineer breakthrough materials with optimized structure-function characteristics [7,8]. As an example, some HEMs with outstanding mechanical properties, including both good strength and ductility, especially at high temperatures, have been developed [9,10]. Among multiple other fields, owing to their exceptional characteristics and huge range of possibilities, HEMs have recently raised great interest for nuclear applications. In this direction, some HEMs have been demonstrated to provide exceptional combinations of thermal neutron absorption cross section, radiation resistance and high temperature mechanical properties [11,12]. In a timely response to the recent progresses in this field, the present mini review article aims at briefly analyzing the irradiation properties of

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HEMs, to summarize their recent advances for nuclear reactors, and to emphasize new and promising potential research directions.

2. Advanced reactors concepts and current state of materials

2.1. Advanced fission reactors

Within a nuclear fission reactor a fissile atomic nucleus (e.g. 235 U or 239Pu) is broken into lighter nuclei releasing a huge amount of energy [1]. The nuclear fission reactor confines and controls this reaction. During atomic fission, the fissile nucleus (fuel) is subjected to neutron bombardment, decaying into fission fragments of unequal mass, releasing γ rays, α and β particles and several fast neutrons with kinetic energies of about 2 MeV [13]. To maintain the reaction, in Gen II and Gen III reactors, the fast neutrons must be slowed down into thermal neutrons (kinetic energy of about 0.025 eV) by a neutron moderator material (H2O or heavy water (DO2). On the other hand, some Gen IV fission reactors may not require moderators and the chain reaction is maintained by fast neutrons owing to the use of highly enriched U or Pu fuels. To control the nuclear chain reaction, the use of neutron absorption elements (control rods) in the core of the reactor is also required. A critical element in the reactor core is the fuel cladding, which stands between the radioactive material and the coolant/moderator [2]. The fuel cladding material is subject to extreme operation conditions and thus must satisfy several design constraints including low neutron absorption cross section, high service temperature, neutron radiation resistance, mechanical strength, creep resistance, toughness, thermal expansion, thermal conductivity and chemical compatibility (corrosion resistance) with respect to fissile products, coolant, moderator and fuel materials. Besides excellent mechanical and chemical properties, cladding materials need to be characterized by low neutron absorption cross-section (transparent to neutrons) to minimize neutron losses (such as Mg, Be, Si, Al, and Zr). Zirconium alloys developed in 1950–70 are the most efficient and used cladding materials in current fission reactors, owing to their low neutron absorption cross-section, their high corrosion resistance, and their notable strength at moderate temperatures (~330 °C) [14]. However, Gen IV fission reactors operate at the much higher temperatures (600–1000 °C) allowed by their advanced coolants: liquid metals, helium gas or molten salts [13]. The current Zr alloys suffer from lack of sufficient high temperature strength and corrosion resistance toward the advanced gas or molten metal coolants. These limitations have triggered massive efforts to develop new high temperature cladding materials [12,15].

2.2. Fusion reactors

Fusion reactors involve probably the most severe operating environment ever realized for a utility-scale power generation system. Today, the nuclear fusion of deuterium-tritium (DT) is considered as the most feasible reaction to be implemented in a commercial fusion power plant. In these reactors, plasma temperatures of about 2×10^8 °C need to be generated to overcome the Coulombic repulsion between deuteron and triton, a challenge not only for plasma physicists but also for materials scientists aiming at the development of durable in-vessel plasma-facing components [4]. In DT fusion reactors, neutrons are produced with an order of magnitude higher energy compared to fission neutrons (14 MeV for DT fusion vs. ~1 MeV for fission). These much higher energies can significantly increase displacement damage per neutron collision in fusion reactors when compared with fission reactors [16]. This high neutron energy also induces much higher H and He transmutation rates (~10–100 appm He/dpa for DT fusion neutrons compared to ~0.1–10 appm He/dpa for fission neutrons) [4]. High H and He transmutation may lead to high temperature helium embrittlement and increased cavity swelling in the structural materials at elevated temperatures, and accelerated embrittlement at low temperatures [17]. Therefore, the in-vessel components in fusion reactors, such as plasma-facing parts, breeding blanket or divertor (exhaust system of plasma), must have superior properties including high melting point, low activation, low sputter erosion, suitable thermomechanical properties, and low tritium retention/co-deposition. Particularly, the 'breeding' of the tritium (3H) fusion fuel by neutrons (n) is carried out through 6Li + n → 3H + 4He reaction [16]. This requires that the materials selected for the tritium breeder blanket have low neutron absorbance to allow passage of neutrons from the fusion core to undergo the breeding reaction. The structural components of the breeder blanket in fusion reactors are expected to operate well above 400 °C, exceeding the working limit of current Zr alloys [14].

Tungsten is the leading candidate for plasma-facing parts owing to its high melting temperature, low erosion rates, high thermal conductivity and small tritium retention [18,19]. Unfortunately, these advantages are coupled with a very low fracture toughness and pronounced embrittlement upon irradiation with neutrons at temperatures below ~800 °C, which significantly restrict the useful operating temperature window and create some difficulties in fabrication [4]. Furthermore, formation of holes, pits and bubbles by He at high temperature (>1400 °C) and blistering by D and He at intermediate temperature (<600 °C) have been observed [20]. These may enhance surface erosion and arguably enhance deuterium/tritium trapping at neutron-induced cavities leading to unacceptably large tritium inventories in the plasma-facing parts.

Extensive research has been carried out by the material science community to develop new materials with suitable properties to meet the harsh requirements of advanced nuclear reactors. Oxide dispersed strengthened (ODS) ferritic-martensitic (FM) steels, Ti_3AlC_2 MAX phase ceramic, multilayer metallic nanocomposites, and SiC/SiC, Si_3N_4- and MgO-based ceramic composites are among the most successful materials developed for advanced reactors [21]. However, none of these materials meet all the requirements of advanced nuclear reactors, or at best, are not economic candidates either from a manufacturing process point of view or due to a reduced working life.

3. HEAs as next generation nuclear materials

3.1. Complex concentrated/high entropy alloys

The evolution of humankind has been driven by the use of new materials and energy forms. Through our history, applied materials have evolved toward more complex compositions that provide improved functionality, e.g. from copper, to bronze, to steel. More complex materials offer additional degrees of freedom both to expand their range of mechanical and functional properties and to finely adjust them toward a particular application. Complex concentrated alloys (CCAs) and particularly high entropy alloys (HEAs) are the most recent breakthrough is this search toward materials with optimum functional properties. While HEAs are typically defined as single-phased disordered solid solution that contain five or more principal elements in an equal or near-equal atomic percentage with no obvious difference between the solute and solvent, CCAs expand even more the material range by including multiphase alloys consisted of three or more principal elements. In fact, CCAs cover both HEAs and medium entropy alloys (MEAs). Among these new materials, CCAs consisted of refractory elements are of great interest for high temperature applications [22,23]. Although still a very small number of refractory HEAs has been studied for nuclear applications, several outstanding and unique properties, such as low neutron cross-section, reduced activation, high temperature strength, and oxidation resistance, have been reported and are being exploited [7,11,12,24,25].

3.2. Current state of CCAs/HEAs as nuclear materials

Recently, CCAs or HEAs consisted of refractory elements have been introduced as promising candidate for advanced nuclear reactors owing to their superior mechanical/chemical properties and apparent resistance to radiation. Complex materials offer additional possibility to

design high radiation resistance materials through tailoring microstructural features such as dense dislocation arrays, nanoscale grain dimensions, finely dispersed precipitates, or nanoscale multilayer interfaces to act as point defect recombination sinks. WTaCrV is an example of a refractory HEA with tailorable microstructure features showing outstanding radiation resistance owing to the formation of Cr- and V-rich second-phase particles at equal mobilities of point defects and their recombination probability [26]. This alloy exhibits a high nano-indentation hardness of 14 GPa with nearly negligible irradiation hardening in the as-deposited (magnetron sputtering) state. Moreover, no sign of irradiation-induced dislocation loops has been detected for WTaCrV even after radiation up to 8 dpa. Reported results clearly suggest that WTaCrV HEA might be a proper candidate for plasma-facing components in fusion reactor, thus it deserves additional investigation.

At present, Zr alloys are the most extensively used cladding material and favored over steels because of their lower thermal neutron absorption cross-section (~0.2 for Zr alloys vs. ~2.0 for steels) [14]. However, Zr alloys may undergo significant oxidation and alpha to beta phase transition during loss of coolant scenarios, which result in ballooning of the cladding tubes and a further reduction in coolant flow [20]. NbTiVZr HEA has been proposed as an accident-tolerant fuel cladding in nuclear fission reactors to replace current Zr alloys [12]. The NbTiVZr HEA developed by King et al. [12] exhibited higher hardness than current available zirconium alloys, but at the cost of higher neutron cross-sections and problematic thermal stability. Further work is needed to investigate the resistance of this HEA to irradiation, especially at elevated temperatures.

Several HEAs consisted of reduced activation elements such as TiVZrTa and TiVCrTa [11], HfTaTiVZr [27], Ta-Ti-V-Zr-X (X = Hf or W) [24], W_xTaTiVCr [28] and TiVCrMnFe [29] have been developed. Generally, these alloys exhibited superior radiation resistance compared to their single elements or binary counterparts. For example, a twofold improvement in the strength and hardness of WxTaTiVCr HEA (compared to pure W and W-based alloys) due to in-situ TiC second phase formation (where C came from the graphite mold during spark plasma sintering) and solid solution strengthening has been reported [28]. HfTaTiVZr HEA exhibited 20% hardening, while a stainless steel specimen exhibited 50% hardening under identical irradiation with 4.4 MeV high-energy Ni^{2+} ions. An excellent irradiation resistance with negligible irradiation hardening and abnormal lattice contraction upon helium-ion irradiation has been observed in BCC structured $Ti_2ZrHfV_{0.5}Mo_{0.2}$ HEA [30].

Apart from the above-mentioned refractory HEAs, several HEAs consisted of transition elements have been also investigated for nuclear applications. The most studies on this group have been concentrated around CoCrFeNi- and Al_xCoCrFeNi-based HEAs irradiated by heavy ions. Table 1 presents a summary of these studies on HEAs and their main findings for nuclear applications. Generally, CCAs or HEAs exhibit better radiation resistance than their pure elements, which is attributed to their compositional complexity, lattice distortion and the associated sluggish diffusion [31–34]. It is reported that the irradiation resistance of Ni-containing HEAs at 500 °C can be highly improved by the number and, particularly, the type of constituent elements [31]. The phase stability of Al_xCoCrFeNi HEA has been also reported to be problematic under irradiation at 500 °C, where decomposition into FCC and B2 or Ni_3Al type nanoprecipitates with L12 ordered structure was observed [35,36]. However, there are still some discrepancies on the microstructural evolution and irradiation resistance among the reported studies, which need to be further investigated. For example, Chen et al. [37] reported similar microstructural evolution (high density of dislocation loops) and irradiation hardening for CoCrFeMnNi and $Al_{0.3}$CoCrFeNi HEAs and 316H, concluding that irradiation damage of fcc alloys is not sensitive to compositional variation and configurational entropy. On the other hand, Kumar et al. [34] reported superior radiation resistance with lower density of small dislocation loops and irradiation hardening for FeNiMnCr HEA compared to commercial single phase Fe-Cr-Ni austenitic stainless steels.

It is widely accepted that materials with BCC structure usually possess higher radiation resistance than FCC structured materials. This argument is also reported to be true for BCC HEAs. The overlap regions of the distribution of migration energies of vacancies and interstitials in BCC HEAs was reported to be much larger than that in the FCC HEAs, resulting in superior resistance to radiation through boosted defect recombination [38]. Therefore, BCC HEAs seem to be more promising candidates for developing next generation materials for nuclear applications.

3.3. Scientific challenges

While complex multicomponent materials offer additional degrees of freedom to tune their mechanical and functional properties, a rational material design and engineering is fundamental to simultaneously optimize the numerous involved parameters. This rational design must be based on an in-depth understanding of underplaying mechanisms, which is still missing [47]. At the time of writing this article, the concept of high entropy phases as a novel direction for extreme environments in nuclear fusion/fission reactors is still in its infancy. Although data on radiation-related properties of HEMs are still very limited, recent progresses have been deliberated to reveal the most prominent challenges facing further development of HEMs for advanced nuclear reactors:

3.3.1. Underlying mechanisms responsible for radiation resistance

The superior irradiation resistance of HEAs was first attributed to the sluggish atomic diffusion owing to their highly disordered solid-solution nature and innately strained lattice, which substantially hinder the evolution of irradiation-induced 0D to 3D defects in the cascade region [15,41]. Similarly, some works argued that the high resistance of HEAs to irradiation may stem from the change in the migration of interstitial defect clusters due to composition complexity and lattice distortion, which intensifies point defects (vacancy-interstitial) recombination in the regions where the defects are generated [32,48]. However, these arguments are counterintuitive because while superior radiation behaviors with increasing compositional complexity have been observed in some multicomponent systems [31,50], the radiation resistance of HEAs is not simply a function of the number of alloying elements and the ensuing lattice distortion [49]. Different studies revealed distinct interactions between cascades, 0D defect clusters, 1D/2D isolated defects, 3D precipitates and sinks in various HEA systems [25,26,33,51,52], as shown in Fig. 1. Besides, the nature of elements and their coordination environments also contribute to the radiation resistance of HEAs, as reported for Co, Cr, Fe and Mn in Ni-containing HEAs [31,44,51]. These may result in different cascades-defects interactions and consequently distinct underlying mechanisms for radiation resistance in different HEAs. However, it is clear that the interactions between radiation and defects are synergized by compositional complexity and alloying elements, providing a wide span for tailoring the irradiation responses of these CCAs. It should be also noted that most studies on the mechanism of irradiation resistance in HEAs have been focused on CoCrFeNi- and AlCoCrFeNi-based systems, while the underlying mechanism in refractory HEAs has remained highly unexplored. Recently, the high radiation resistance of $Ti_2ZrHfV_{0.5}Mo_{0.2}$ refractory HEA was attributed to its high vacancy concentration, which is believed to act similar to the oxide in ODS steel alloys. That is to say, the fundamental understanding of radiation resistance in HEAs, especially refractory HEAs, is still far from being clear.

3.3.2. High temperature neutron irradiation resistance

At present, most studies on irradiation of HEAs compare their properties with elemental counterparts or conventional alloys, which makes it hard to evaluate whether or not they have superior performance than state of the art FM steels. However, our comparison of irradiation resistances in term of irradiation hardening and swelling

Table 1
The most prominent reported HEMs for nuclear applications and their main properties.

HEAs Category	Alloy system	Crystal structure	Irradiation condition	Main findings	Ref.
Reduced activation	W-Ta-Cr-V	bcc	1 MeV Kr + 2, 1.6–8 dpa at RT and 800 °C	High radiation resistance at RT and 800 °C, No radiation-induced dislocation loops, low irradiation hardening	[26]
	$W_xTaTiVCr$	bcc + TiC + C15 Laves phases	No irradiation test	Twofold higher hardness and strength than those of pure tungsten	[28]
	Ta-Ti-V-Zr-X (X = Hf or W)	bcc		High temperature hardness	[24]
	TaTiVZr	bcc1 + bcc2 + bcc3	2 MeV V^+ Fluence: 2.26 × 10^{15} cm^{-2} at 500 °C	Hardness 7.41 GPa (TiVZrTa) and 6.83 GPa (TiVCrTa),	[11]
	TaTiVCr	bcc + C15 Laves phase		No measurable irradiation hardening,	
	TaTiVZrHf	bcc	4.4 MeV Ni^{2+} Fluence: 1.08 × 10^{17} cm^{-2}	Partial amorphization at ~35 to 40 dpa, Irradiation hardening of 20%	[27]
	TiVCrMnFe, $Si_{0.1}TiVCr_{0.5}Fe$	C14 Laves phase + B2/A2	No irradiation test	Phase instability at 1200	[29]
Low neutron cross-section	Nb-Ti-V-Zr	bcc	No irradiation test	Decomposition into alpha (hcp), C15 and nano-scale bcc upon aging at 700 °C, Higher hardness and neutron cross-section than current Zr alloys	[12]
	MoNbCrVTi	bcc		Hardness: 494.4 ± 7.7 Hv, yield strength: 1281 MPa, fractured strain: 9.4%	[39]
	MoNbCrZrTi	bcc + C15 Laves phase		Hardness: 552.9 ± 8.6 Hv, yield strength: 1454 MPa, fractured strain: 2.7%.	
Other refractories	$Ti_2ZrHfV_{0.5}Mo_{0.2}$	bcc	3 MeV He+ at 600 °C, 0.5–3 × 10^{16} cm^{-2}	Negligible irradiation hardening, lattice constant reduction after irradiation, high density lattice vacancies act like ODS steel	[30]
	TiVNbTa	bcc	2 MeV V^+ Fluence: 2.26 × 10^{15} cm^{-2} at 500 °C	Hardness: 5.86 GPa, Irradiation hardening of 0.66 GPa (8%)	[11]
	Zr-Hf-Nb	bcc	2 MeV electron beam	Stable structure up to 10 dpa (at 25 °C) and 50 dpa (at −170 °C), HEAs are self-healing and highly irradiation resistant	[15]
	TiZrNbHfTa	bcc	5 MeV He^{2+} Fluence: 4.4 × 10^{17} cm^{-2} (0.8 dpa) at RT	Increase in yield and ultimate tensile strength without loss in ductility after irradiation	[40]
Transition elemets	$Al_xCoCrFeNi$ (x = 0.1, 0.75, 1.5)	fcc (x = 0.1), B2 + fcc (x = 0.75), B2 + A2 (x = 1.5)	3 MeV Au ions Fluences: 1 × 10^{14} to 1 × 10^{16} cm^{-2} at RT	x = 0.1: no precipitates even at ~43 dpa, x = 0.75, 1.5: different precipitates after irradiation	[41]
	$Al_{0.1}CoCrFeNi$	fcc	3 MeV Au ions, Fluence: 6 × 10^{15} cm^{-2} (~31 dpa), at 250–650 °C	Defect clusters such as dislocation loops and long dislocations enriched in Ni/Co and depleted in Fe/Cr. Defects density decreased and their size increased with increasing temperature	[42]
	$Al_{0.3}CoCrFeNi$			Dislocation loops at 250 °C and 350 °C Dislocation loops + faulted loops at 500 °C Dislocation lines and networks + B2 precipitation at 650 °C	[35]
	$Al_{0.12}CoCrNiFe$		3 MeV Ni^{2+} Fluence: 1 × 10^{17} cm^2 (~100 dpa) at 500 °C	Decomposition into FCC and $L1_2$-Ni_3Al type nanoprecipitates	[36]
	CoCrFeNi		400 and 1250 kV, electron dose rate ~ 5 × 10^{18} $e{\cdot}cm^{-2}{\cdot}s^{-1}$ at 400 °C	Elliptical Frank or polygonal perfect loops, >40 times slower defect growth than the linear defects of pure Ni	[25]
	CoCrFeNi		1.5 MeV Ni^+ Fluences: 4 × 10^{14} and 3 × 10^{15} cm^{-2} at 500 °C	Composition complexity and lattice distortion localize defect migration and increase defect recombination, improving swelling resistance	[32]
	CoCrFeMnNi		3 MeV Ni^+ Fluence: 5 × 10^{16} cm^{-2} at 500 °C		
	CoCrNi, CoCrFeNi, CoCrFeMnNi		3 MeV Ni^{2+} Fluences: 5 × 10^{16} cm^{-2} (~53 dpa) at 500 °C	CoCrFeNiMn showed 40 times higher swelling tolerance than Ni, More influence on swelling reduction for Fe/Mn than Co/Cr, Higher irradiation hardening for HEAs (11%–16%)	[31]
	CoCrFeMnNi $Al_{0.3}CoCrFeNi$		1 MeV krypton at 300 °C	Similar microstructural evolution and irradiation hardening for HEAs and 316H, Irradiation damage of fcc alloys is not sensitive to compositional variation and configurational entropy	[37]
	CoCrFeNi, CoCrFeMnNi,		3 MeV Ni^{2+} Fluence: 5 × 10^{16}/cm^2 at 500 °C	By increasing compositional complexity, the density of faulted loops increase and the radiation-induced segregation is suppressed	[33]
	CoCrFeMnNi CoCrFeNiPd		3 MeV Ni^{2+} 5 × 10^{16}/cm^2 at 420–580 °C	An order higher of swelling by increasing temperature from 420 to 580 °C. Pd have a stronger suppression effect on void and dislocation loop growth than Mn	[43]
	(18Cr-27Fe-27Mn-28Ni) and (15Cr-35Fe-15Mn-35Ni) (wt %)		1 MeV Kr++ at −223 and 500 °C	Small defect clusters and faulted dislocation loops at −223 °C, interstitial dislocation loops at −500 °C, Variation in atomic size and mass don't necessarily reduce point defect production	[44]
	18Cr-27Fe-27Mn-28Ni (wt%)		3 to 5.8 MeV Ni ions, 0.03 to 10 dpa	No phase instability and voids after irradiation to 10 dpa at 400–700 °C,	[34]

(*continued on next page*)

Table 1 (*continued*)

HEAs Category	Alloy system	Crystal structure	Irradiation condition	Main findings	Ref.
			RT to 700 °C	Lower radiation-induced solute segregation and defect cluster size compared to austenitic alloys,	
	18Cr-27Fe-27Mn-28Ni (wt%)		Neutron irradiation flux of 8.57–8.9× 10^{14} n/cm^2.s (0.1–1 dpa) at 60 °C	Irradiation hardening: 60% (0.1 dpa) and 105% (1 dpa), Similar behavior for HEA and austenitic alloys in mechanical performance and phase stability	[45]
	C-doped $Fe_{38}Mn_{40}Ni_{11}Al_4Cr_7$		5 MeV Xe^{23+} (1, 3.8 and 10 dpa) at RT	C doping suppressing defects formation and evolution through increase in lattice distortion and migration energy of interstitial atoms	[46]

revealed that the properties of ion-irradiated HEAs are similar to those of neutron-irradiated advanced FM steels (Fig. 2a, b). HEAs show better irradiation hardening behavior at room temperature and a comparable performance at high temperatures, as shown in Fig. 2a. The void swelling behavior of HEAs is also as low as that of advanced FM steels. The excellent irradiation properties observed in HEAs already at their very initial stage of development and optimization for nuclear applications draw a promising vision for further researches in this field. However, the majority of irradiation studies on HEMs used heavy ions to investigate the interactions between cascades and defects. While ions

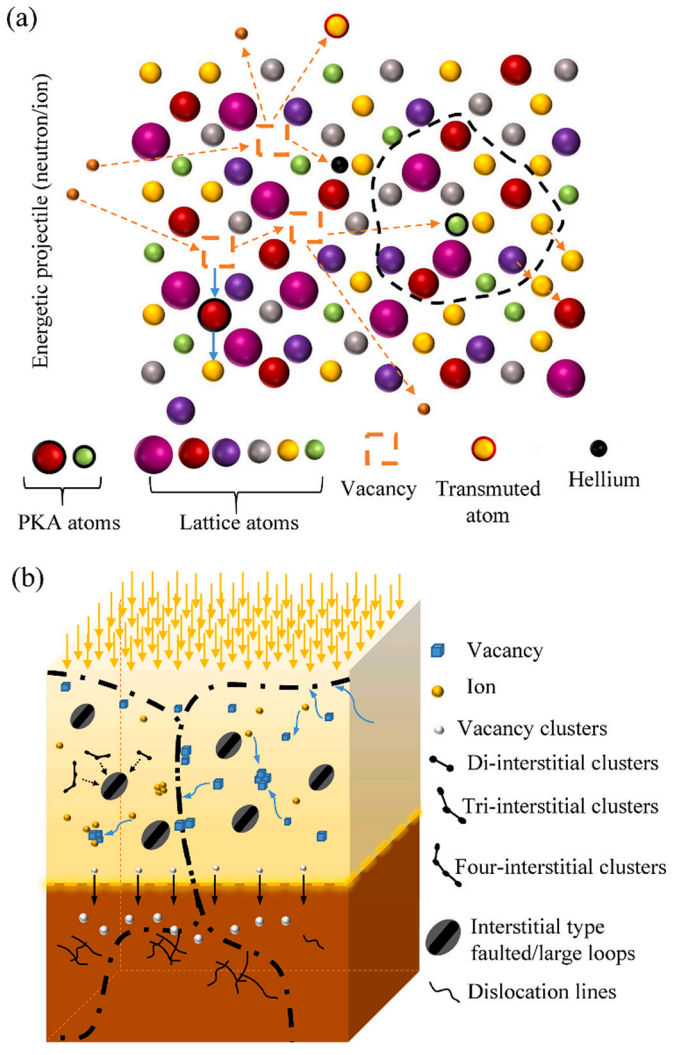

Fig. 1. Schematic illustration of defect evolution and distribution in HEAs. (a) Atom-projectile interaction showing elastic scattering of projectile ions and the ensuing knock-on atoms (PKAs) in different direction. (b) Defect evolution and distribution in HEAs as a result of ion irradiation.

radiation remains a useful experiment to study the microstructural evolution of HEMs, neutron irradiation may result in different interactions [45], which need to be performed ultimately to confirm their radiation resistance for nuclear applications. Long-term phase stability and thermal aging under neutron irradiation is another challenge to be furhter investigated.

4. Perspectives

In order to bring HEMs one step closer to the real application in nuclear reactors, we prioritize here three directions that need to be pursued (Fig. 3).

4.1. Data on post irradiation thermal, mechanical and corrosion properties

Recent studies provided better understanding about microstructural evolutions of HEAs upon irradiation at room and high temperatures. When juxtaposing HEAs against conventional materials in terms of radiation resistance and thermal stability, the superiority of HEAs seems to become a reality. However, the data on physical and mechanical properties of HEAs, especially refractory HEAs, after irradiation is still very limited. Moreover, the studies on radiation resistance of HEAs have been largely focused on microstructural evolution and radiation hardening. While there is still seldom data on post-radiation tensile properties of HEAs [45], the long-term mechanical behaviors such as creep and creep-fatigue properties also need to be evaluated [57]. The corrosion behavior and degradation mechanisms in aggressive environments of advanced nuclear reactors have remained unexplored. Particularly, these properties are synergized by displacement damage and H/He transmutation (in fusion reactors), which result in irradiation induced embrittlement and deterioration in Charpy and toughness properties. The current micro-mechanical models of mechanical properties would be a useful tool to extrapolate experimental data to the real in-reactor conditions, if they can be extended for HEAs. Besides, the manufacturing and joining processes of HEAs for relatively intricate geometries such as breeding blankets is another challenge. Finally, the fabrication process and properties of HEAs need to be compared with commercial alloys such as Zr-, W-alloys or FM steels to determine whether or not they are promising candidates for advanced nuclear materials.

4.2. New high entropy irradiation resistance alloys

Materials selection for advanced nuclear reactors need to simultaneously satisfy several critical features including irradiation resistance (over 200 dpa), creep resistance, high temperature hardness, dimensional stability, hot corrosion resistance, and resistance to flaking, swelling, and thermal fatigue. Developing materials with multi-tier properties regarding all these requirements, which are beyond the performance of current nuclear materials, has been one of the long-standing challenges of the materials engineering community. Considering the nearly infinite compositional space of high-entropy alloys, the above-mentioned researches may be considered as just the starting point to

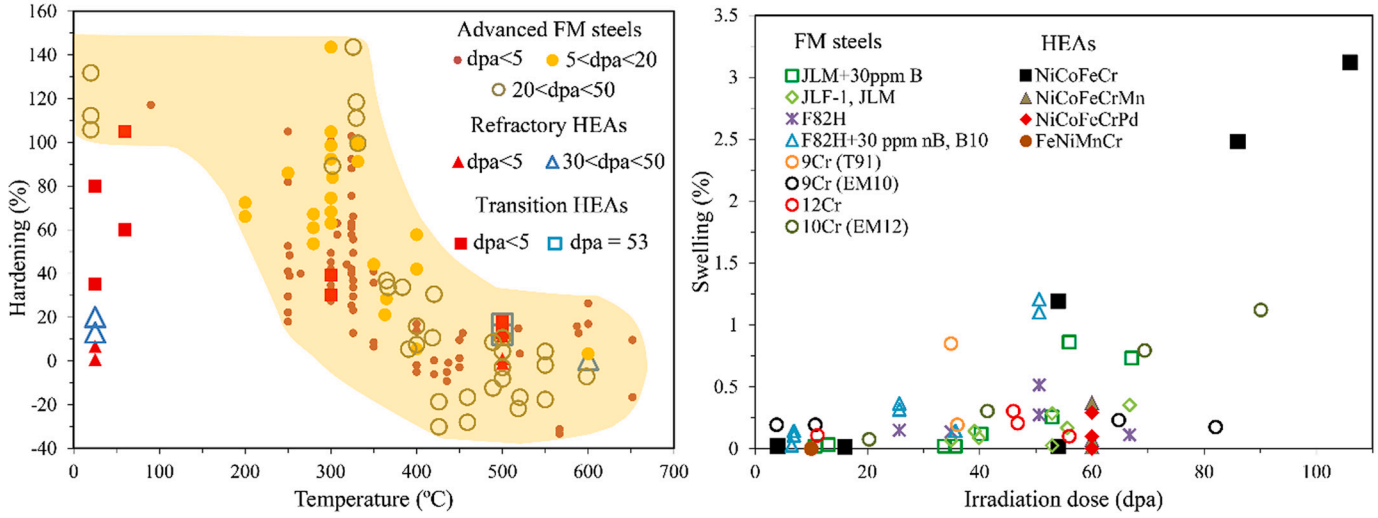

Fig. 2. The irradiation hardening and swelling of the reported HEAs compared with advanced FM steels. The hardening values for FM steels and HEAs were calculated from yield strength [53–56] and hardness [11,26,27,30,31,37,45], respectively. The swelling values are void swelling for both FM [53] and HEAs.

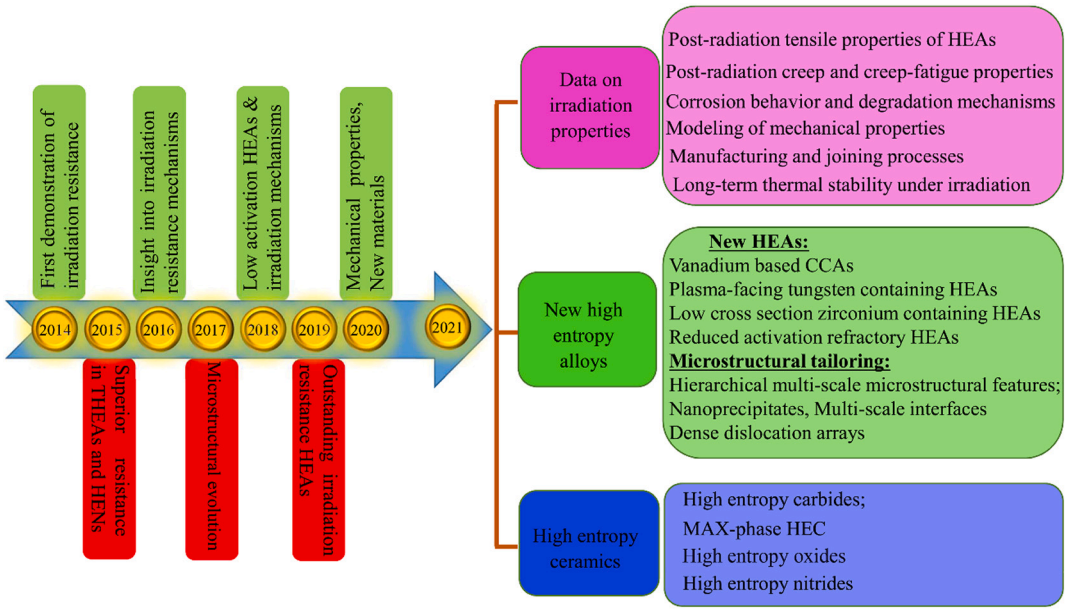

Fig. 3. Main progresses in HEMs for nuclear applications and possible research directions for 2021.

develop superior HEAs for next generation nuclear applications. There are still numerous new high entropy compositions, especially low neutron cross section zirconium containing HEAs, plasma-facing tungsten containing HEAs, vanadium containing CCAs, and reduced activity elements refractory HEAs which need to be more investigated. Besides, novel alloying design and microstructure-tailoring to induce high-density point defect recombination sinks through hierarchical multi-scale microstructural features such as nanoprecipitates, dense dislocation arrays and multi-scale interfaces are other promising research directions. Oxide dispersed strengthened HEAs (ODS-HEAs) [58,59] may be such a tailorable microstructure HEAs, where dispersed Y_2O_3 particles in ODS-HEA (especially BCC-HEAs) become effective sinks for pinning point defects and helium atoms, suppressing their migration and coalescence leading to swelling.

4.3. High entropy ceramics

The concept of high entropy ceramics (HECs) is relatively new, being introduced in 2015 [60]. The interest in radiation resistance of HECs has been recently aroused, as high irradiation resistance and phase stability were observed in $(Zr_{0.25}Ta_{0.25}Nb_{0.25}Ti_{0.25})C$ after 20 dpa irradiation at 500 °C [61], although some high entropy nitrides have been already reported to exhibit superior irradiation behavior [62,63]. However, considering the large number of high entropy carbides reported to date and their promising properties such as high melting point and hardness [64], additional investigation in their irradiation behavior is worthy and fundamental to determine their potential applications in nuclear reactors. We also suggest high entropy oxides (HEOs) and MAX phase HECs (MAX-HECs) as other promising materials for nuclear applications. To the best of our knowledge, there is no study on MAX-HECs neither for advanced nuclear reactors nor for other applications. However, different high entropy carbides have been successfully developed including (HfZrTaNbTi)C [65] and (TiZrNbTaW)C [66]. Therefore, it is expected that high entropy carbides with MAX formula ($M_{n+1}AC_n$), where M lattice sites satisfy the criteria of HEMs, may be stable single phases. MAX phase ceramics consist of alternating layers of close-packed M-atoms, A atomic layers, and X-atoms, where M stands for an early transition metal, A is a group IIIA or IVA element, and X refers to carbon

or nitrogen filling octahedral sites. The atomic-scale alternating metallic monolayer and ceramic multilayers act as interfacial sinks resulting in good radiation resistance [67]. Moreover, the irradiation behavior of HEOs has not been studied yet. Therefore, exploring novel HECs and their irradiation behavior may lead to a breakthrough in ceramics and nuclear materials as they synergize the unique characteristics of ceramics and the properties of high entropy phases in a single material.

5. Conclusion

In this paper, the operating environment and materials requirements for advanced fission and fusion nuclear reactors were first described. Subsequently, the current state of research within irradiation behavior of HEAs was summarized. Some scientific challenges facing further researches on irradiation behavior of HEAs were also discussed. Our evaluation regarding the irradiation behavior of HEAs at their very initial stage of development and optimization draw a promising vision for their successful implementation as plasma-facing components, breeding blanket and divertor in fusion reactors and fuel cladding in G IV fission reactors. Finally, further studies on post-irradiation thermal, physical and mechanical properties of HEAs, new irradiation resistance HEAs and HECs such as carbides, oxides and MAX-HECs were enumerated as the main directions for further studies.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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