Atomic-level Heterogeneity and Defect Dynamics in Concentrated Solid-Solution Alloys

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ABSTRACT

Performance enhancement of structural materials in extreme radiation environments has been actively investigated for many decades. Traditional alloys, such as steel, brass and aluminum alloys, normally contain one or two principal element(s) with a low concentration of other elementals. While these exist in either a mixture of metallic phases (multiple phases) or solid solution (single phase), limited or localized chemical disorder is a common characteristic of the main matrix. In sharp contrast to the traditional alloys, recently developed single-phase concentrated solid solution alloys (CSAs) contain multiple elemental species in equiatomic or high concentrations with different elements randomly arranged on a crystalline lattice. Due to the lack of elemental predictability in these CSAs, they exhibit significant chemical disorders and unique site-to-site lattice distortions. While it has long been recognized that specific compositions of traditional alloys have enhanced radiation resistance, it remains unclear how the atomic-level heterogeneity affects defect formation, damage accumulation, and microstructural evolution. Such knowledge gaps have been a roadblock to future-generation energy technology. CSAs with a simple crystal structure, but complex chemical disorder are ideal systems to understand how compositional complexity influences defect dynamics, and to fill the knowledge gaps with focus on electronic- and atomic-level interactions, mass and energy transfer processes, and radiation resistance performance. Recent advances of defect dynamics and irradiation performance of CSAs are reviewed, intrinsic chemical effects on radiation performance are discussed, and future directions are suggested.

Key words: chemical disorder; concentrated solid-solution alloys; lattice distortion; energy landscapes; defect dynamics; microstructure evolution; irradiation effects

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1. Introduction

Ever since ancient civilization, development and improvement of metallic alloys with better structural strength or improved functionalities have repeatedly changed the world and enriched the breakthroughs that are provided to meet human needs. Useful alloys have typically comprised multiple phases, with one or two dominant elements modified by small additions of other elements. Conventional approaches typically take a material that empirically has good properties, and make small changes in composition and microstructure to achieve more desired performance, such as improved radiation tolerance. For discussion purposes in this work, most of these alloys being studied in the past or used in various applications are termed as ***traditional alloys***. Such traditional alloys are also commonly referred as dilute alloys, with the major element as a solvent and alloying elements as a solute.

In sharp contrast to traditional alloys, concentrated solid solution alloys (CSAs), consisting of two to five (or more) elemental species all at high concentration, have recently attracted increasing attention and intensive research effort [1-3]. The newly developed multi-component systems with five or more elements, typically near equiatomic composition, are commonly termed high entropy alloys (HEAs), wherein the configurational entropy is higher than the entropy of melting of most common metals [4-6]. Instead of ordered intermetallics from classical physical metallurgy, a direct consequence of thermodynamic stabilization of some high-entropy phases is a reduction of the thermodynamic driving force towards oxidation and phase transformation. Both face centered cubic (fcc) and body-centered cubic (bcc) CSAs, including HEAs, with a strong tendency to solid solution strengthening have been produced. These ***non-traditional alloys*** exhibit strong resistance to softening (high strength and low plasticity) at high temperatures, and excellent tensile strength at low temperatures, which makes them candidate materials for many potential applications, including high-temperature thermal stability and hardness [7-9], improved fatigue, strength, ductility, and fracture resistance [3,10,11], improved irradiation resistance [2,12-14] and excellent corrosion and wear resistance [5].

Intense radiation in nuclear fission and fusion power systems transfers energy to electrons and atoms in the material, and produces defects. Structural materials in advanced nuclear reactor components, such as iron-based alloys (the primary basis for structural materials), must demonstrate long-term stability and tolerance to radiation damage at elevated temperatures over long lifetimes. It is known that the accumulation of defects may ultimately compromise the material's strength and performance lifetime. Historically, alloy development in traditional alloys with improved radiation performance has been focused on addition of alloying elements or nanoscale features with complex microstructures to mitigate damage. To move beyond the current knowledge and incremental radiation resistance property improvements in traditional alloys, we must understand the roles of all constituents in alloys and their atomic-level heterogeneity effects on defect evolution in a radiation environment.

The current opinion and developments in this article will focus on single-phase CSAs with HEAs as part of the family. The constituent elements in these CSAs are distributed randomly on a crystal lattice, such as fcc, bcc, or hexagonal close-packed (hcp). While retaining a simple macroscopically crystalline structure, such random occupancy of different elemental species (extreme ***chemical complexity***) creates unique site-to-site lattice distortions and locally disordered chemical environments, leading to extreme intrinsic complexity at the electronic and atomic levels [2,12,15,16]. In extreme cases such as in HEAs, no element will have the same nearest and second nearest neighbor environment [2,15]. Such unusual lattice distortions have demonstrated significantly improved radiation resistance attributing to the high atomic-level stresses facilitating rapid recrystallization and preventing extended dislocation formation.

Recent research has focused on how alloy complexity in single-phase CSAs affects defect dynamics and microstructure evolution by varying the number, type and concentration of alloying elements [2,12-14,17]. This article reviews compositional effects on radiation performance in traditional alloys and informs on current progress of radiation effects in CSAs, including unique energy landscape of CSAs and atomic-level understanding on defect dynamics at both short- and long-time scales. Challenges and future directions are discussed. In this special issue, the *Physical Metallurgy of Concentrated Solid Solutions from Low-Entropy to High-Entropy Alloys* is reviewed by Yeh *et al.*, the *Phase Stability,*

Physical Properties and Strengthening Mechanisms by Bei *et al.*, the *Thermodynamics of Concentrated Solid Solution Alloys* by Gao *et al.*, the *Mechanical properties of solid solution high- and medium-entropy alloys* by George *et al.*, and the *Fundamental Deformation Science in Multiphase High Entropy Alloys* by Liaw *et al.*

2. Traditional alloys: compositional effects on radiation performance

Alloying elements at low-concentrations into pure metals is the traditional approach in the long history of alloy development, and is widely used to achieve desired materials properties, such as better yield strengths and enhanced radiation tolerance. In many dilute solid solutions, numerous experimental observations, with some specific examples reviewed below, have shown that substitutional additions at a certain amount can significantly improve or degrade radiation performance. While many possible explanations are proposed, no unified underlying mechanisms and validation are currently available.

A study of the Ni-Cu system displays a remarkable resistance to void formation under irradiation [18,19]. In pure nickel samples, voids formed throughout the entire damage range under Ni irradiation, but only appeared at the near-surface region and at the peak damage depth under Cu irradiation. The effect of alloy additions on radiation response was performed later by the same group [20] in pure nickel and two Ni-Cu alloys with pre-implanted He. The results show that the density of both dislocation loops and helium bubbles increases with increasing copper content, while the size decreases. The authors speculated that nanoscale Cu particles might exist in the Ni-Cu alloys to disperse vacancies and gas atoms, thereby suppressing the swelling. This statement was not confirmed due to the limited detection resolution of transmission electron microscopy (TEM) available at that time. With today's knowledge, one question to ask is whether such a significant difference in radiation behavior results from the nano-scale precipitates, from alloying effects (interplays between Ni and Cu) in the solid solution form, or from the combination of the two.

In the Ni-Al binary alloy system with Al levels ranging from 1.1 to 13.3 wt%, irradiation responses were investigated at temperatures ranging from 400 to 650 °C in the EBR-II fast reactor [21]. The irradiation-induced density changes were found to strongly depend on both Al content and irradiation temperature. The results clearly show that the progressive addition of Al decreases the swelling toward a saturation level at lower irradiation temperatures. At higher temperatures, there is a tendency for swelling to increase again at the higher Al levels. Although the importance of Al content is clearly observed, the underlying mechanisms to explain these observations are missing. In this study, the Al concentration varied from a few percent in a dilute alloy to a more concentrated solid solution alloy with an Al concentration over ten percent. Defect and mass transport in dilute alloys have been studied intensively, the transport property in concentrated solid-solution alloys is, however, much less understood [14,22,23]. A key challenge for the Ni-Al work is to understand alloying effect on migration barriers and paths for both interstitials and vacancies as a function of Al concentration and temperature, especially near the percolation threshold of mass transport.

Physical, chemical and mechanical properties of metallic solid solutions are often thought to be affected by a difference in atomic size between the solvent and solute elements [24] in traditional alloys. The effects of volume size factor of solute atoms (a measure of the dilation caused by a solute) have been studied [25] in He-irradiated Ni-based alloys at 500°C. The swelling results of pure Ni, Ni-Si, Ni-Co, Ni-Cu, Ni-Mn and Ni-Pd alloys show that volume size factors strongly affect the radiation-induced swelling. The number density of bubbles as well as the mean size increased with the volume size factor. Such observations imply that both the irradiation-induced point defects and the mobility of helium are influenced by elemental species and chemical disorder, which calls attention to elemental effects or chemical effects on defect dynamics.

Strong compositional dependence to irradiation response is also observed in the V-Fe binary and V-Fe-Ti ternary systems [26]. A systematic increase in cavity size was observed with increasing Fe concentration. The void swelling of pure V is low after irradiation to ~11 displacements per atom (dpa) at a range of temperatures. Alloying low concentration of Fe (5%) leads to a dramatic increases in swelling,

up to 30%. Addition of low levels of Ti to the V-5Fe alloy leads to suppression of swelling. In each case, the authors report that the solutes remain in the solution. A similar result has been reported more recently for various Ti contents in V-Ti alloys and Fe contents in V-Fe alloys under He irradiation [27]. Increase of Ti concentration in V-Ti alloys leads to reduced swelling, which is attributed by the authors to local regions of compression resulting from the oversized Ti atom in V lattice. On the other hand, when undersized Fe atoms replace V atoms, it is believed that sites for sinks of interstitial atoms are formed to interact with He. The arguments based on the impact of under-sized and over-sized solutes for the observed sensitivity clearly demonstrate the importance of atomic-level understanding of elemental effects (localized tensile or compression stress resulting from the lattice distortion) to material performance.

Commercial high-strength Ni-Cr systems were developed in the 1950-1960s for blades of jet engine turbines. Properties of some Ni-Cr alloys have been studied, aiming to determine the possibility of their use as structural materials for nuclear reactors [28-30]. While the absence of gas-vacancy pores in these alloys indicated a low concentration of vacancies and low mobility of transmutation He, the low dislocation density suggested a low concentration of interstitial atoms. The low defect concentration (vacancies and interstitials) presented from these studies may, however, be viewed as an outcome of tailoring chemical complexity to control defect evolution through suppressed defect production and enhance recombination at an early stage – a path forward for designing special structural alloys with improved radiation resistance [2,12].

There are many studies on the Fe-based alloys that have indicated significant impacts of composition and chemistry on defect production and evolution. The Fe-Cr binary alloys are a base for low activated ferritic-martensitic steels used widely as structural materials for fission reactors and currently being considered as candidate materials for future fusion reactors. A series of studies of irradiation behavior of Fe-Cr alloys and pure Fe has been undertaken in an attempt to elucidate the basic mechanisms of defect formation, void swelling and low temperature irradiation-induced embrittlement in ferritic-martensitic steels [31-36]. Microstructural changes induced from radiation damage in Fe and Fe-Cr alloys have also been investigated as a function of irradiation temperature, ion/neutron fluence, and Cr content under triple-beam irradiation (D^{2+}, He^{+}, Fe^{+}) [37]. The composition dependence of swelling on Cr concentration is explained in terms of different binding interactions between Cr solute atoms and irradiation-produced vacancies, as well as the difference in sink strength of microstructural features. More recently, the evolution of radiation damage in Fe and Fe-Cr alloys under heavy-ion irradiation has been investigated [38,39]. Dynamic observations are carried out under an electron microscopy where the evolution of damage and the early stages in damage development show that, although small (2-4 nm) dislocation loops first appeared at doses between 10^{12} and 10^{13} ions cm^{-2} in all samples, the number of loops retained depended strongly on the foil orientation in pure Fe, but not in Fe-Cr alloys, with different Cr content. The *in-situ* observations show hopping of very mobile ½<111> loops in pure Fe under ion and electron beam irradiations, and that many ½<111> loops easily glided to the foil surface. Hopping of dislocation loops is particularly pronounced in ultra-pure Fe, but occurs much less frequently in Fe-Cr alloys. Lower loop mobility in Fe-Cr alloys is observed and attributed to possible pinning effects by Cr atoms. One may wonder that if such pinning effects are a key control of defect dynamics, which may be the most effective way to achieve the maximum density of pinning sites per unit volume. Considering the random arrangement of multiple elemental species in CSAs, such atomic-level alternation would meet the requirement that each atom can be in fact viewed as a pinning site — the most effective way to create the maximum density of pinning sites per unit volume [2].

Changing the number of constituent elements and various compositions in more complex alloys, defect production and damage evolution shows new features. In fcc alloys, point defect processes in neutron irradiated Ni, Fe-15Cr-16Ni and Ti-added modified SUS316SS are reported recently [40]. Void growth is discussed on the basis of the interactions of vacancies and interstitials with defect clusters. The growth behavior of interstitial-type dislocation loops (I-loops), stacking fault tetrahedra (SFT) and voids is found to be quite different among these specimens. While I-loops are developed at lower temperatures in Ni than in Fe-15Cr-16Ni and modified SUS316, more swelling occurs in Ni than in Fe-15Cr-16Ni, and

no voids are observed in modified SUS316. There is a significant difference in defect structures between Fe-15Cr-16Ni and modified SUS316 due to low weight concentration of alloying elements of Ti, Si, Mo, Mn and C. The growth of SFT detected in Fe-15Cr-16Ni and modified SUS316 is explained by a change in the dislocation bias of SFT resulting from the absorption of alloying elements. These studies on alloys with increased compositional complexity have indicated significant impacts of alloying effects at the elemental level on defect production and evolution.

As a brief summary of the literature review on radiation response in traditional dilute alloys and some concentrated alloys, compositional complexity has shown clear influence on defect dynamics and radiation responses. The lack of a unified fundamental description of the effects of the compositional complexity on defect processes and irradiation performance poses a significant roadblock to alloy development for applications in extreme radiation environments. All the above experimental observations are pointing to a more general base: *substitutional solid solutions with increasing **chemical complexity** in terms of local disordered chemical environments and unique site-to-site lattice distortions may have a profound effect on fundamental processes in determining defect production and damage evolution.*

3. Non-traditional alloys: unique single-phase concentrated solid-solution alloys

3A. Concentrated solid solution alloys with tunable chemical complexity

CSAs compose of multiple elemental species randomly arranged on a simple crystalline structure. In these CSAs, the chemical complexity can be achieved by controlling the number, type, and concentration of the constituent elements. The composition of such CSAs can be at or near equiatomic or at concentration with one or two elemental species in large variation within the solubility limits, as noted in **Fig. 1**. These CSAs with different elements coupled inimitably show distinct properties at the level of electrons and atoms and allow a systematic study of defect dynamics and irradiation performance with increasing complexity.

While CSAs encompass HEAs, they can also been considered as subsystems of HEAs, such as subsets of $Ni_{25}Cr_{25}Fe_{25}Co_{25}Pd_{25}$ (NiCrFeCoPd) or $Ni_{25}Cr_{25}Mn_{25}Fe_{25}Co_{25}$ (NiCrMnFeCo). Model CSAs that we focus in this review include alloys from simple binaries (e.g. $Ni_{50}Fe_{50}$ (NiFe), $Ni_{50}Co_{50}$ (NiCo), $Ni_{40}Fe_{60}$, $Ni_{60}Fe_{35}$, $Ni_{80}Fe_{20}$, $Ni_{80}Pd_{20}$ and $Ni_{80}Cr_{20}$) and ternaries (e.g. $Ni_{33}Co_{33}Fe_{33}$ (NiCoFe), $Ni_{33}Co_{33}Cr_{33}$ (NiCoCr) and $Ni_{40}Fe_{40}Cr_{20}$) to more complex quaternaries (e.g. $Ni_{25}Cr_{25}Mn_{25}Co_{25}$ (NiCrMnCo), $Ni_{25}Cr_{25}Fe_{25}Co_{25}$ (NiCrFeCo) and $Ni_{25}Mn_{25}Fe_{25}Co_{25}$ (NiMnFeCo)) and quinary HEAs of NiCrFeCoPd and NiCrMnFeCo. To avoid confusion, the CSAs with equiatomic composition will be denoted only by the corresponding element symbols, as indicated in parentheses.

Of central importance for this set model alloys shown in **Fig. 1**, achieved by randomly replacing Ni atoms with various metal species at different concentration, is that these alloys form at equiatomic composition or high concentration, yet crystallize in fcc solid solutions with a high degree of chemical inhomogeneity. In these alloys, the random arrangement of multiple elemental species on a crystalline lattice results in the lack of long-range order or translational periodicity, in some extreme cases lack of short-range order as well. Since these alloys span a broad spectrum of substitutional disorder, it is therefore possible to understand how electron, phonon, and magnon systems are impacted by modifying chemical complexity; substantially reduce electron, phonon, and magnon mean-free paths; modify

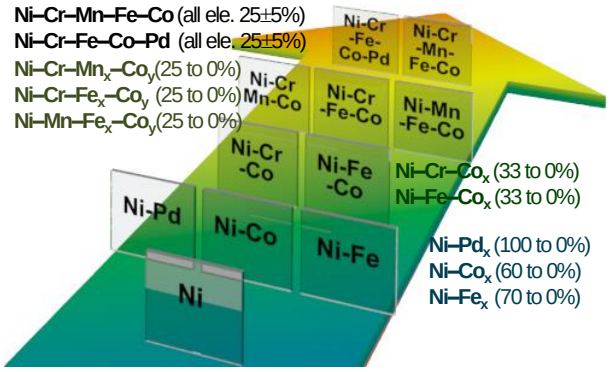

Fig. 1 Tunable CSAs where the range of possible variation for certain elements within the solid solution is noted in brackets. Extreme chemical disorder by altering alloy composition may pave the way for new design principles of functional alloys for energy applications.

coupling strengths; and create complex defect formation energy and migration barrier landscapes. Two distinctive intrinsic properties are expected: (1) disordered local chemical environments that significantly enhance electron-electron interactions and affect energy dissipation [2,12,15,16], and (2) unique site-to-site lattice distortions that lead to atomic level compressive or tensile stress and complex energy landscapes, which affect defect migration [12-14,22,23] and exceptional mechanical properties [3,10,11].

To quantify the first distinctive property, experimental and modeling studies have been carried out on alloy systems with increasing chemical disorder (pure Ni metal and alloys of NiCo, NiFe, NiCoFe, NiCoCr, NiCoCrFe, NiCoCrFeMn and NiCoCrFePd) to understand effects of compositional disorder on the electronic structure, electron mean free paths, short-range order, and magnetic moments [2,12,15,16]. *Ab initio* Korringa-Kohn-Rostoker Coherent-Potential-Approximation (KKR-CPA) calculations [41] are used to describe the ground state electronic and magnetic structure, and to reveal the effects of chemical disorder on the underlying electronic structure. The results show that the Bloch spectral functions display two characteristic features: little disorder in the majority states in the alloys containing only ferromagnetic elements such as NiCo, NiFe, NiCoFe, and significant smearing in both minority and majority states in alloys NiCoCr and NiCrFeCo where ferromagnetic Ni, Fe, and Co couple antiferromagnetically with Cr [2,12,16]. A significant reduction of electrical and thermal conductivity of SP-CSAs is predicted for the alloys with mixed ferro- and anti-ferromagnetic interactions, and is confirmed with electrical resistivity and thermal conductivity measurements. Substantial electronic-level modification and significant reduction of energy dissipation through coupled electronic and magnetic subsystems in these model alloys are discussed and summarized elsewhere [2,12,16].

In this review, we focus on the second distinctive property to reveal the role of chemical complexity on atomic processes – effects of atomic level disorder on energy landscapes. Most of the standard conceptual tools for traditional alloys implicitly assume that the system is close to a periodic solid. For example, vacancy and interstitial motion models assume that most of the lattice is homogeneous with the same activation energies with the presence of discrete trapping sites in dilute alloys due to minor alloying elements or lattice imperfections. Modeling CSAs requires the development of new theoretical constructs and effective assembling techniques. While formation and migration energies have been studied in ordered Ni metal, the effects of compositional disorder are unclear. In the concentrated solid solutions, the traditional electron band theory, phonon transport and diffusion implicitly applied to a system nearly periodic may fall apart. The symmetrically variation of elemental species, composition and local disorder provides unique controls to understand defect physics (defect energetics and complex energy landscape unique to CSAs) that may lead to radiation resistance.

3B. Defect Energetics Unique to CSAs

To understand the effects of random site occupancies of different elemental species, atomic-scale properties resulting from lattice distortions of the fcc concentrated alloys are characterized. The atomic-scale properties, such as point defects, rely greatly on their local environments. In particular, the properties of defects are greatly affected by the chemical inhomogeneity presented in these CSAs [42]. The disorder comes from both the chemical disorder induced by random arrangement of different elements (no element has the same neighbors) and the displacement fluctuation (lattice distortion) caused by the different characteristics of elements. Such disorders cause the environment-dependent energetics of defect formation and migration to be fundamentally different from pure materials and traditional dilute alloys. As a result, the formation and migration energies of vacancies and interstitials have a distribution, rather than having a single value as is generally thought in the dilute alloys. While the formation energy measures the difficulty to create the defect, and the distribution in CSAs suggests that the defect could exist over a large energy range. Moreover, the distribution of migration barriers will change the diffusion mechanism of these defects. In addition, it is highly likely that the distribution of different kinds of defects will overlap, which governs the degree to which the defect populations may separate. For example, an overlap in the distribution of migration energies indicates similar diffusion coefficients and thus a prolonged interaction time between different kinds of defects.

Although *ab initio* calculations have become standard methods to investigate the defect energies, the disorder in these CSAs possess great challenges to such modelling efforts. Two methods can be used to tackle the disorder presented in these systems. One is the coherent potential approximation (CPA) method [2,15,41] that is a single-site, mean-field theory capable of describing the composition disorder, including configurationally averaged single-site charge density, magnetization density, density of states, and total energy. However, the CPA method does not allow consideration of the effects of local lattice distortion or displacement fluctuations. While defects can be modeled as an additional (dilute) species, the distribution of formation energies and migration energies that results from local environmental effects cannot be obtained using the CPA method. In addition, it cannot be utilized to study the migration of defects due to its fixed lattice sites. The other approach is the supercell approach by constructing the special quasi-random structures (SQS) [43] that considers the structure details by relaxing the position of atoms, though the computational cost is much higher due to the large supercell required to simulate the defect properties. In this method, the effects of configurational averaging are often ignored as this information is assumed to be included in the SQS structure. Nevertheless, the supercell models provide detailed information about the defect structure, and thus are suitable for describing the distribution of defect energies.

Classical molecular dynamics (MD) and atomistic Monte Carlo (MC) methods based on interatomic potentials are on the other hand able to consider the disorder by computing plenty of structures and obtain configurational averages due to their much lower computational cost than DFT. In addition, it can be used to study the long-term evolution of defects at different temperatures. The defect evolution predicted by these potentials is closely related to the atomic-scale defect energies, since these energies determine the relative stability of different defects. For example, a high diffusion coefficient is always observed for the defects with lower formation energies, as they provide the diffusion channel to facilitate the defect migration. Since MD results depend sensitively on the interatomic potential used, it is therefore critical to validate the reliability of the potentials for predicting defect evolutions.

Ab initio calculations based on supercell method with a 108-atom SQS cell have been employed to characterize the distribution of defect formation and migration energies in CSAs [42]. In pure Ni, there are six possible interstitial configurations, i.e. octahedral, tetrahedral, crowdion as well as [100], [110] and [111] dumbbells. Among them, the [100] dumbbell is the most stable interstitial configuration with the lowest formation energy of 4.27 eV. The results for NiCo, NiFe, $Ni_{0.8}Fe_{0.2}$ and $Ni_{0.8}Cr_{0.2}$ show that the formation energies for vacancies are mostly higher than in pure Ni, while those for dumbbell interstitials are lower than in pure Ni (4.27 eV). The distribution of migration energies for vacancies and interstitials starts to overlap with increasing disorder from $Ni_{0.8}Fe_{0.2}$ to NiFe, suggesting an unexpected equal mobility in the solid solution phase. This effect is the most prominent for NiFe, suggesting that the replacing Ni with Fe to form solid solution may have a notable influence on the defect energetics. Significantly enhanced irradiation resistance is reported from the ion irradiation

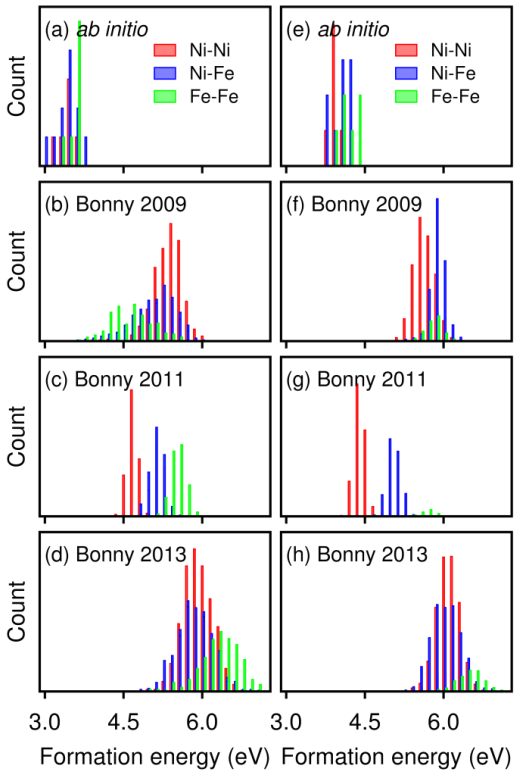

Fig. 2 Formation energy of a [100] dumbbell in NiFe (left column) and $Ni_{0.8}Fe_{0.2}$ (right column) determined from *ab initio* calculations (a and e) and three EAM potentials: Bonny2009 (b and f), Bonny2011 (c and g) and Bonny2013 (d and h). There are 26 data points in the *ab initio* results. Adapted from Fig. 2 in Ref. 42

experiments for NiFe compared with pure Ni and NiCo [2,12], which indicates a potential link from modified defect energetics to radiation performance. The *Ab initio* calculations also suggest that diffusion barrier of interstitials in $Ni_{0.8}Cr_{0.2}$ is found to be smaller than that in NiFe and $Ni_{0.8}Fe_{0.2}$, an indication of faster migration of interstitials in $Ni_{0.8}Cr_{0.2}$.

The *ab initio* results for interstitial dumbbells in NiFe and $Ni_{0.8}Fe_{0.2}$ are provided in **Fig. 2**, together with the results calculated from three embedded atom method (EAM) potentials developed by Bonny *et al.* [44-47]. To distinguish different versions, these potentials are denoted by the year they were developed, as Bonny2009 [44], Bonny2011 [45], and Bonny2013 [46]. The results from the EAM calculations are determined from a 2048-atom supercell to obtain a full sampling of the local environments of dumbbells. The dumbbell is introduced at each site, and the dumbbell structure is picked out after relaxation to calculate the formation energies. The results show that the formation energies from the *ab initio* calculations are relatively small in both NiFe and $Ni_{0.8}Fe_{0.2}$. However, all three EAM potentials predict larger formation energies with different distributions. The formation energy of the Fe-Fe dumbbell is the largest for Bonny2013. Moreover, Bonny2011 results in three separate distributions for the Ni-Ni, Ni-Fe, and Fe-Fe dumbbells, whereas Bonny2009 and Bonny2013 give largely mixed formation energies. In NiFe, while the formation energies for Fe-Fe dumbbells are smaller from Bonny2009 as compared to the Ni-Ni and Ni-Fe dumbbells, an opposite trend is observed from Bonny2013. Compared with the *ab initio* results, Bonny2013 generates a similar distribution for all dumbbells, although their energies are highly overestimated. It is worth noting that the small supercell (108 atoms) used in the *ab initio* calculations tends to overestimate the formation energies of interstitials due to the possible interactions between the interstitial and its periodical images. The smaller formation energies of interstitials in NiFe are, therefore, not affected by the choice of supercells.

The diffusion barrier is calculated from Nudged elastic band (NEB) method. The migration of Ni vacancies has a lower energy barrier than the migration of Fe vacancies, by hopping among the lattice sites through exchange with Ni or Fe atoms, respectively, in both NiFe and $Ni_{0.8}Fe_{0.2}$. For interstitials, it is found that $Ni_{0.8}Cr_{0.2}$ has smaller diffusion barriers for Ni and Cr interstitials compared to NiFe and $Ni_{0.8}Fe_{0.2}$. The migration energy in NiFe and $Ni_{0.8}Fe_{0.2}$ is larger than that in pure Ni, which will give rise to slow diffusion of interstitials in these two alloys. An important finding is that the migration energies of vacancies and interstitials in NiFe have a region of overlap. The overlapping may greatly enhance defect annihilation in NiFe and make it more resistant to ion irradiation [12].

The defect energetics discussed so far is basically obtained at 0K by neglecting the temperature effect. Although it provides important insight into the particular feature of defect properties in CSAs, the defect behaviors are likely to be affected by lattice vibration arising from finite temperatures. Unfortunately, it is extremely computationally costly to address the vibrational properties by *ab initio* calculation, as it requires accurate phonon calculations. Moreover, the activation energies for defect diffusion are also temperature dependent. In this case, MD simulations that allow the consideration of both temperature and local energy profiles are especially important.

3C. Complex Energy Landscape Unique to CSAs

In the NEB calculations, the diffusion barrier is calculated from the energy landscape by fixing the initial and final state. This is useful when the initial and final state can be defined accurately. However, these states are hard to be determined in actual irradiation environment that is far from non-equilibrium condition. The problem can be solved by means of molecular dynamics simulations, in which the defect is allowed to find its own migration pathway according to local environment and energy landscape. Both *ab initio* molecular dynamics (AIMD) and classical MD simulations can be used, in principle, to study the diffusion properties at finite temperature. However, as revealed from static NEB calculations, the diffusion of defects in these CSAs is more difficult than in pure Ni. As a result, much longer simulation time is required so that a large number of defect jumps is counted to capture the long range diffusion behaviors in CSAs This is a great challenge to MD simulations, especially for an AIMD, which requires a high computational cost.

The diffusion of interstitials in NiFe, NiCo and NiCoCr is studied by AIMD within a 108-atom supercell plus an interstitial. The typical simulation time is about 30 ps. In order to speed up the diffusion process, different temperatures up to 1800K have been employed. Due to the sluggish diffusion in these CSAs, the number of defect jump observed in such a short time scale is in the range of 300-1000 dependent on temperature. Most of the jumps for interstitials occur in the form of dumbbells along the direction of [1/2,1/2,0]. The tracer diffusion coefficients are extracted from the calculated mean squared displacement (MSD). The results suggest higher diffusion coefficients of Ni in NiFe, Co in NiCo, and Co in NiCoCr. Detailed analysis indicates that the interstitials in these materials diffuse in the form of specific dumbbells: Ni-Ni and Ni-Fe in NiFe; Ni-Co and Co-Co in NiCo; Co-Cr in NiCoCr. This is closely related to their formation energies. As displayed in **Fig.2**, *ab initio* results show that Ni-Fe and Ni-Ni dumbbells have lower formation energies than Fe-Fe. Therefore, the diffusion of interstitials in NiFe is mainly through the Ni channel that leads to higher diffusion coefficient of Ni. Similar arguments are also applicable to NiCo and NiCoCr. It seems that these systems all have distinguishable formation energy distributions for different dumbbells. As a result, there is always one type of dumbbells that dominates in these CSAs. This explains a preferable diffusion of a corresponding species. In fact, these observations can be traced back to the structure of CSAs. In NiFe, it is found that the first nearest neighbor distance is the largest for Fe-Fe, suggesting that Fe has larger radius than Ni in *fcc* NiFe. Ni-related dumbbells, therefore, exhibit lower formation energies and preferable diffusion. The structural analysis for NiCo and NiCoCr also predicts the same trend. Although this property is element-dependent, the preferable diffusion provides evidences to modulate the distribution of formation energies and thus manipulate the interstitial flow in various CSAs by tailoring their chemical complexities.

Mass transport is essential to materials performance, such as elemental segregation, phase stability, thermal aging, mechanical stress, and radiation performance. In CSAs, while the properties of defects are expected to be greatly affected by the chemical inhomogeneity (Section 3B), the complex energy landscapes are anticipated to affect mass transport mechanisms and pathways. Classical MD can extend to very long simulation time compared to AIMD, and it is widely used to study mass transport. Most previous studies focus, however, on conventional dilute alloys, barely different from a pure element material from the viewpoint of compositional complexity. Mass transport in CSAs has not drawn sufficient attention until recently valuable information of interstitial and vacancy transport mechanisms is obtained in NiFe [22] from long timescale simulations. The most striking finding is that vacancies and interstitials in NiFe migrate through different alloy components. Comparing in Ni, the results in NiFe indicate that replacing Ni with Fe, alloy chemistry leads to sluggish diffusion and elemental segregation. It is found that the diffusion frequency in the equiatomic binary alloy is reduced significantly relative to the pure Ni metal. In the binary alloy, interstitials move via Ni sites, while the vacancies primarily hop among the lattice sites through exchange with Fe atoms. The results will allow prediction of segregation behavior under thermal aging, where vacancy sinks are depleted, as Fe flows in the opposite direction to vacancies. Moreover, it is also argued that Fe depletion near interstitial sinks will be significantly enhanced by Ni enrichment under irradiation where interstitials and vacancies are produced directly. Such modification of transport pathways is an important feature in concentrated alloys, including HEAs. The work [22] points out that the Fe migration path should be broken, inhibiting vacancy diffusion if the Fe concentration is below the fcc site percolation level of ~21 at%. Likewise, interstitial diffusion may switch off when the Ni migration path is blocked with decreasing Ni concentration locally. In addition, by introducing additional alloying elements into the migration pathways, it is expected that both the Fe and Ni contiguous paths may be close that both vacancy and interstitial diffusion can be significantly suppressed. An implication is that manipulating the chemical complexity may enable one to separately affect interstitial or vacancy diffusion.

4. Defect dynamics and irradiation performance of concentrated solid-solution alloys

4A. Materials response to radiation energy deposition

The evolution of radiation-induced defect concentrations can be described in simplified terms by three competing processes: the 1st term containing defect production from collision cascades; the 2nd term containing subsequent vacancy-interstitial recombination within the diffusion volume during the cascade events; and the 3rd term including extended defect clusters formed from the accumulation of the cascade damage within the host matrix, as well as absorption by nano-scale features such as additional phases, interfaces, grain boundaries, and precipitates. Both the 1st and 2nd terms in such a simplified description are short-time processes up to a few picoseconds (the ballistic phase shown in **Fig. 3**), while the 3rd term includes the processes over a much longer time scale (the kinetic phase illustrated in **Fig. 3** and much longer time processes).

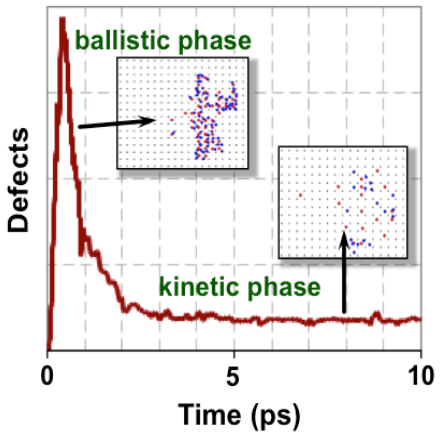

Fig. 3 Schematically showing generation of point defects forming a peak during the ballistic phase followed by vacancy-interstitial recombination during the kinetic phase leaving behind few surviving defects.

A collision cascade can be viewed as an ultra-fast phase transition with complex thermodynamic and kinetic behavior. The incoherent, high-energy motion of atoms in a collision cascade affects the transport of vacancies and interstitials, both are expected to be strongly influenced by the local energy landscapes. Random site occupancies and associated lattice distortions can create large fluctuations of the lattice potential between different lattice sites that modify atom diffusion. Such effects may be utilized hypothetically to suppressed defect production, resulting from enhanced recombination of interstitials and vacancies created from cascade events (integration of 1st and 2nd terms). Due to the extreme chemical disorder and lack of long-range ordering in complex CSAs, the energy landscape will be highly heterogeneous and new theoretical approaches are needed.

It has long been observed that, compared to their pure metal counterparts, traditional alloys with specific compositions have improved radiation resistance, as reviewed in Section 2, and recent research on radiation damage mitigation has focused on the 3rd term through the introduction of a large number of inhomogeneities at nanometer and micrometer level, such as oxide dispersion strengthened (ODS) steels or layered structures. Lack of fundamental understanding of electronic and atomic level mechanisms in the first two terms, as well as evolution of extended defects in the 3rd term due to the complex potential energy landscapes in CSAs, hinders the possibility to design materials intrinsically resistant to radiation damage. It is highly disable to take advantage of property enhancements of concentrated alloys to extrapolate beyond our knowledge from traditional alloys, by tuning chemical disorder, to design alloys intrinsically resistance to radiation damage**.** Meeting this challenge demands an understanding of the role of each constituent element and the composition complexity, so that ultimately it is possible to suppress primary defect production and delay damage accumulation in extreme radiation environments.

Enhancement of radiation tolerance performance in CSAs is different from approaches in traditional dilute alloys relying on altering minor elements or modifying microstructures, one hypothesis is to modify alloy complexity to control defect dynamics at the early stage of radiation damage, and ultimately reduce surviving defect concentrations and enhance radiation tolerance at a later stage. In other words, by tuning chemical complexity to control energy dissipation and defect evolution, it may be possible to significantly reduce the number of surviving defects (the 1st and 2nd terms). Simultaneously, defect dynamics and various energy dissipation processes can be similarly tuned to be more localized, thus enhancing defect absorption at the extended defects and consequentially forming less undesirable damage (processes involved in the 3rd term). Such modified processes (http://edde.ornl.gov/) would delay damage accumulation and lead to more intrinsically radiation-robust alloys.

The tunable chemical complexity, the static defect energetics and transport properties, and complex energy landscapes were reviewed in Section 3. In this section, possible effects of chemical complexity to minimize the 1st term, maximize the 2nd term, and modifying the 3rd term are discussed. The

discussions focus on the non-equilibrium defect kinetics during and after the cascade collisions, as well as during a long-term accumulation.

4B. Defect production and damage accumulation

Recent advances have shown possibilities of controlling defect dynamics at their early stages, including both ballistic phase and kinetic phase, as schematically shown in **Fig. 3**, by changing the compositional complexity of CSAs. Modeling activities, advancing quickly, have benefitted from the availability of comprehensive knowledge and high-performance codes. *Ab initio* theory, time-dependent density functional theory (TD-DFT), AIMD, and classical MD simulations have revealed how alloy complexity can alter energy dissipation (the first distinctive property described in Section 3A) in the electronic and atomic subsystems [48-51], thereby offering the possibility of enhanced defect recombination or self-healing radiation resistance. Increasing experimental activities are evident in recent literatures [2,12-14,23], including the successful growth of large single crystals, the integrated experiments and modeling predictions [2,12,13,52-57], and the collaborative execution of well-defined irradiation experiments and microstructural characterization to evaluate compositional effects on radiation response [12-14,17,23,55-59].

4B-1. Computational challenges and approaches developed

Modern materials science relies heavily on using a multiscale combination of computational methods to study both equilibrium and nonequilibrium effects. With respect to phase stability and defect properties, quantum mechanical density functional theory (DFT)-based first principles calculations are advanced to examine the relative energetics and determine defect formation energies in CSAs (see Section 3B) [60]. They can also be used to provide the necessary inputs for constructing classical interatomic potentials to carry out MD (see examples in Section 4B-2) or Metropolis Monte Carlo (MMC) simulations, which can be used to simulate atom dynamics and thermodynamic properties, respectively. MD simulations are, however, limited to nanosecond time scales, while MMC does not have a time scale at all. To access longer time scale processes, e.g. defect migration, kinetic Monte Carlo (KMC) methods may be used. The required inputs, such as defect migration rates, can, at least in principle, be obtained from DFT and/or MD simulations.

For concentrated solid solution alloys, the use of all these techniques has particular challenges. In DFT, which is limited typically to a few hundred atoms, as noted above it becomes difficult to obtain a representative sample of atom configurations due to the necessity to mix atoms of many types in many different configurations. Classical MD or MMC simulations, on the other hand, require as the crucial physics input of interatomic potentials. These are usually constructed by fitting a relatively simple functional form or set of cubic spline nodes into a set of experimental and DFT data of different phases with possible elastic, defect and surface properties. However, for CSAs so far little experimental data is available, and the difficulties on carrying out DFT calculations also hamper the setup of generating inputs for MD. Also, it is not obvious into which kind of configurations and with what procedure to fit all the mixed-element interactions. Finally, for setting up KMC simulations, one would need in principle to know defect migration rates for all possible atomic configurations forming a defect. To illustrate the complexity of this, one can consider just the simplest possible defect, a single vacancy. Such a vacancy in an fcc crystal is surrounded by 12 neighbors, and hence in a high-entropy alloy of 5 elements has 5^12 possible surrounding configurations. Even with current computer capacity, tabulating this number of configurations is practically impossible, and hence other methods, such as on-the-fly barrier calculations, need to be used.

Notwithstanding these challenges, progress has been made on developing simulation techniques for CSAs on all the simulation levels, especially advances in *Ab initio* calculations as discussed in Section 3B and MD simulations in Section 4B-2 and 4B-3. In the following, we briefly review some of these approaches that are uniquely applicable to CSAs.

4B-2. Development of interatomic potentials

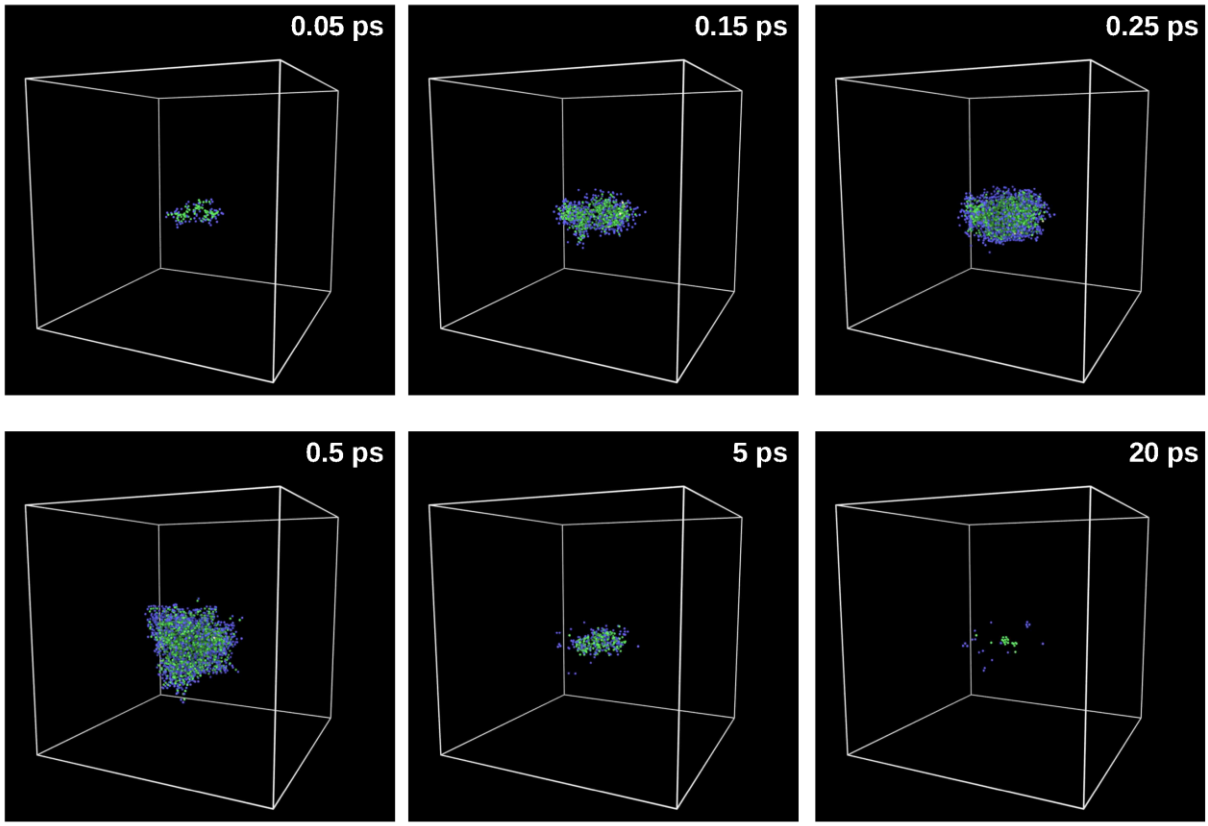

Fig. 4 Defect formation in a 10 keV self-recoil induced cascade in NiCrFeCo. The green spheres indicate the position of vacancies and the purple ones are the interstitials. The white box shows the entire simulation cell.

Cascade events often produce many interstitials and vacancies. To assess defect dynamics, atomistic simulations with empirical interatomic potentials are a common approach. Recent MD work [61-63] has identified a problem of short-range forces in radiation damage modeling. In **Fig. 2**, the *ab initio* results in the Ni–Fe alloys are compared to those calculated from available empirical interatomic potentials [44-47], and the results indicate that these empirical potentials are insufficient to describe the energetics of interstitials in Ni–Fe alloys. For examples, the results from the 2013 Bonny potentials show that replacing Ni with Fe decreases primary damage production, consistent with experimental observations [2,12], while using the 2009 Bonny potential leads to an opposing conclusion – increase in damage production. The issue is attributed to difference in the interatomic potentials at short interatomic distances that are typically inaccurately modeled [62,63].

In displacement cascades, extreme pressures and temperatures arisen from the high-energy recoils, bringing atoms closely together where the interatomic distances become very short, ~ 1-2 Å. At such distances, the interatomic interactions are poorly described by most interatomic potentials commonly used for atomistic modeling. [62,63]. Atomic level interactions at larger separation distances are controlled by the equilibrium properties of the material, which are used to parameterize the interatomic potentials to ensure reliable results of atomistic simulations in near equilibrium conditions. The common practice is to transition from the equilibrium potential to the repulsive universal potential by Ziegler, Biersack, and Littmark (ZBL) at small atomic separation distances.

During the early phase of collision cascades, the interatomic separation of the two colliding atoms can be much smaller than the equilibrium lattice parameter, and the interatomic potentials fitted to equilibrium properties tend to significantly underestimate the potential energy of the colliding dimer. Recent studies [61-65] identify this significant and yet underappreciated issue in joining the equilibrium

potentials to the ZBL potential. Different approaches with an arbitrary function within an arbitrary region of space are commonly used for such a transition, which may result in an unphysical prediction. The lack of a unified approach to describe the joining to short-range forces may be problematic for comparing defect production between different potentials.

Several *ab initio* based methods have been utilized to calculate short-range interactions of atoms, including those in high-pressure states [63,65]. Accurate representation of the forces involved is possible by refitting classical interatomic potentials. The recent work has demonstrated that using first-principles techniques it is possible to accurately describe the energy of interatomic interactions in this transition region and the atomic collisions taking place within the short interatomic distances play a significant role in determining survival primary damage production. These recent studies [61-63] indicate that the development of potentials for CSAs is essential.

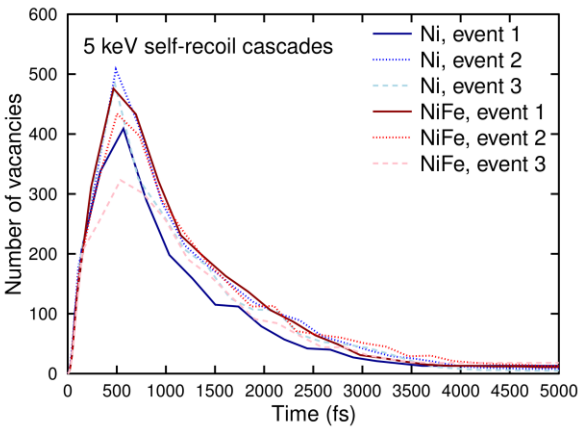

Fig. 5 Defects as a function of time in cascades induced by 5 keV self-recoils in bulk Ni and NiFe. Defects form a peak during the ballistic and heat spike phases of the cascade development, and follow by vacancy-interstitial recombination during the recrystallization phase leaving behind few surviving defects. For both materials, three different recoil events that differ only in the initial direction of the recoil are shown to illustrate the stochastic fluctuations in defect formation.

4B-3. Primary damage formation from cascade event within the ballistic phase

Molecular dynamics simulations have been used extensively to understand the time dependence of damage production in collision cascades [13,53,62,63] induced by keV-energy ions or recoils. These simulations consistently show that in metals, there is violent damage production initially by ballistic collisions (**Fig. 3** ballistic phase), which in turn lead to formation of a so-called heat/thermal spike. However, after a few ps, much of the damage recombines during the kinetic phase and much longer time evolution. In metals, this relaxation effect is particularly strong, leading to a reduction in number of defective atoms of about two orders of magnitude (see **Figs. 4** and **5**). The results in **Fig. 5** were obtained with the interatomic potentials of Zhou et al [66]. The underlying mechanism is that pure metals have a very strong capability to recrystallize. In semiconductors and insulators, the recombination effects are much smaller, roughly a factor of two due to the possibility to create amorphous damage pockets.

The picosecond time scale defect creation behavior that could be expected for high-entropy alloys is not *a priori* clear. Although pure metals do exhibit strong recombination, on the other hand many metal alloys can be made amorphous (becoming bulk metallic glasses), and these remain amorphous during irradiation, even exhibiting increasing degrees of disorder. Some simulations of collision cascades in concentrated solid solution alloys known to be stable experimentally do show consistently that the initial damage production in them (the 1st and 2nd terms) is very similar to elemental metals. This is illustrated in **Fig. 5**, which shows that the time dependence in Ni and NiFe is fairly similar, and the fluctuations between individual cascades is larger than the difference between the materials. Simulating the damage production systematically in 100 different single cascades showed that, at least in the interatomic potentials of Zhou et al [66], the damage production in the alloys is on average slightly higher than those in the pure element Ni. However, the difference is fairly small, within ~ 30% between Ni and the alloy that showed the highest damage (NiFe). Some studies of the damage production in individual cascades show that the number of remaining defects after the cascade cooling down phase in initially pristine lattice is practically identical, at least in the cases of Ni, NiFe, NiCo, NiCoFe and NiCoCr [13,53] the amount of defects (vacancies + interstitials) produced by a single 5 keV cascade in the corresponding pristine materials averaged among 100 PKA events. In other words, no damage reduction is observed in

the 1st and 2nd terms. Hence the experimentally observed major differences between damage production in elemental solids and the concentrated solid solution alloys may be sought on longer-term development during the defect buildup or mobility phase (See Section 4C). It is worth pointing out that some studies [13] show no reduction on primary damage production at low fluences, others have indicated significant reduction [2,61,67].

Irradiation damage processes are conventionally simulated by giving a primary knock-on atom (PKA) kinetic energy that is dissipated through elastic collision events, where high PKA energies may lead to a cascade or a few sub-cascades of elastic scattering collisions. The evolution of such radiation-induced defects is the result of the production and instant recombination (1st and 2nd terms) as well as diffusion and accumulation of the defects over time that can be broken down primarily into two stages, i.e., ballistic stage (up to ~ 2ps) and kinetic stage (after a few ps), as shown in **Fig. 3**. A different approach has been applied to CSAs in MD simulations to study point defect interactions at very high concentrations [52, 54]. Instead of creating Frenkel pairs via time-consuming ballistic recoil events in MD cascade simulations as shown by the peak in **Fig. 3**, arbitrary concentrations of Frenkel pairs randomly distributed in a thermalized system can be introduced at the start of the simulation. This approach may be considered as being defect driven, with a focus on capturing the evolution of point defects, such as those created by low-energy ballistic events (e.g., electrons and protons), those that survive single or multiple cascade events, or those that survive a melt-quench process due to extreme electronic energy deposition along a high-energy heavy ion path. The advantage of the method is that relatively long MD simulation times can be achieved because the very short time steps required to simulate the high-energy ballistic defect production process are eliminated. In this approach, microstructure evolution is accelerated or driven by the larger Frenkel pair concentration. Relatively large vacancy and interstitial clusters can be obtained by the diffusion and aggregation of individual point defects [52, 54]. The disadvantage is that the processes inherent to more energetic ballistic events, such as the effects of shock waves [62,63], high displacement densities [67], and thermal spikes [67], which may affect defect production, are not captured. Also not captured are the concentrations or dose dependences of phase transformations, such as amorphization in ordered intermetallic compounds, or the slow evolution of microstructure when Frenkel pairs are added one-by-one with time.

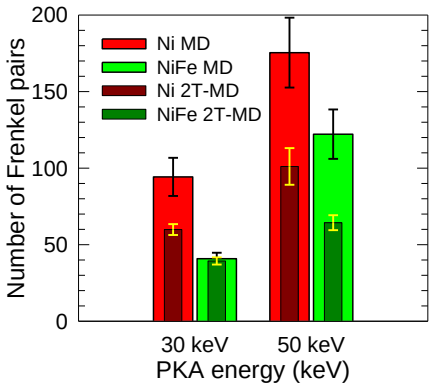

Fig. 6 Number of defects averaged over 12 PKA events (30 and 50 keV Ni), for classical MD simulations where kinetic energy is treated as nuclear energy loss, and for cascades where the electronic stopping is included in a 2T-MD model. The standard error is indicated. Adapted from Fig. 1 in Ref. 67.

MD simulations of high-energy Ni ion cascades (a few ten keV Ni ions) have been carried out in Ni and NiFe with and without consideration of electronic energy loss and e-ph coupling. The electronic effects are incorporated in the MD simulation using a two-temperature MD (2T-MD) model that couples the electronic and atomic subsystems based on their thermal transport properties (e-ph coupling parameter and specific heat) obtained from first principles calculations [67]. The results in **Fig. 6** illustrate the number of surviving defects (sum of interstitials and vacancies) at the end of the simulation time for 30 and 50 keV Ni cascades averaged over 12 events in Ni and NiFe. The predicted damage in NiFe is significantly lower than in Ni for both simulation approaches, opposite to the results from the 5 keV cascaded simulations as discussed earlier [13,53]. The effect of the electronic stopping is more profound in the higher energy cascades, and the energy returned to the lattice via the e-ph interactions enhances defect recombination, which is more evident in the 50 keV NiFe

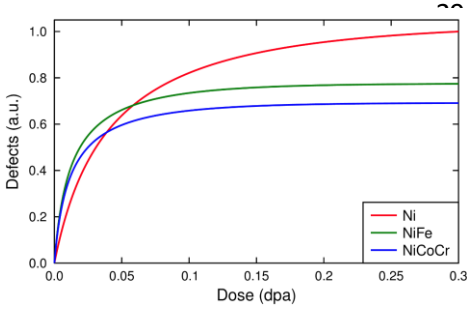

Fig. 7 MD results of damage accumulation in Ni, NiFe, and NiCoCr. The defects are scaled to the amount of defects in pure Ni.

case. The electronic interactions affect not only the amount of damage produced in the system, but also the way the defects are arranged into clusters. More isolated defects are predicted from the 2T-MD simulations.

It is demonstrated that electronic effects, especially at higher energies, can affect the damage level and the defect configuration. Reliable description on defect production from cascade events within picosecond timescale is of great importance to predict defect evolution and long-term performance, and research advances are highly desired to better describe short-range interatomic interactions, the quench of a collision cascade (therefore the degree of agglomeration of vacancies and interstitials), and initial conditions for subsequent microstructure evolution.

4B-4. Defect production and damage accumulation during the kinetic phase

Computational work has provided insight into how compositional differences alter kinetic evolution of defect structures (3rd term) from overlapping cascade simulations [13,53]. Overlapping cascades by molecular dynamics is the most straightforward way to simulate damage buildup, i.e. running first the evolution of the development of one collision cascades, then taking the end result of this cascade as starting position for another running cascade. Since each MD cascade simulations is typically run on time scales of the order of 100 ps, and the simulation cell sizes are of the order of 10 nm, this approach will strongly overestimate the irradiation flux, and ignore thermal defect migration that occurs between cascades [13]. On the other hand, experiments comparing damage production at 30 and 300 K in metals showed fairly similar damage structures, indicating that such an approach nevertheless can be good as a first approximation to study damage buildup.

MD simulations at 300 K reveal significant differences in damage accumulation between pure Ni and the alloys of NiCo, NiFe, $Ni_{0.8}Fe_{0.2}$ and $Ni_{0.8}Cr_{0.2}$ that are consistent with ion channeling results showing slow damage accumulation in alloys. Simulations suggest that alloying elements modify the short-range interatomic interactions and reduce thermal conductivity [2,12]. Consequentially, chemical complexity may result in prolonged lifetime of the thermally enhanced recombination stage, suppress the formation of large extended defects in alloys due to more localized defect migration as they are not as energetically favorable as in Ni. Radiation-induced damage accumulation in $Ni_{0.8}Fe_{0.2}$ and $Ni_{0.8}Cr_{0.2}$ was compared with Ni using MD simulations based on the Bonny 2013 potential [46] to assess possible enhanced radiation resistance [53]. The results show that the defect evolutions are remarkably different in $Ni_{0.8}Fe_{0.2}$ and $Ni_{0.8}Cr_{0.2}$ alloys than in the pure Ni system. The total number of point defects produced under the same dose in $Ni_{0.8}Cr_{0.2}$ and

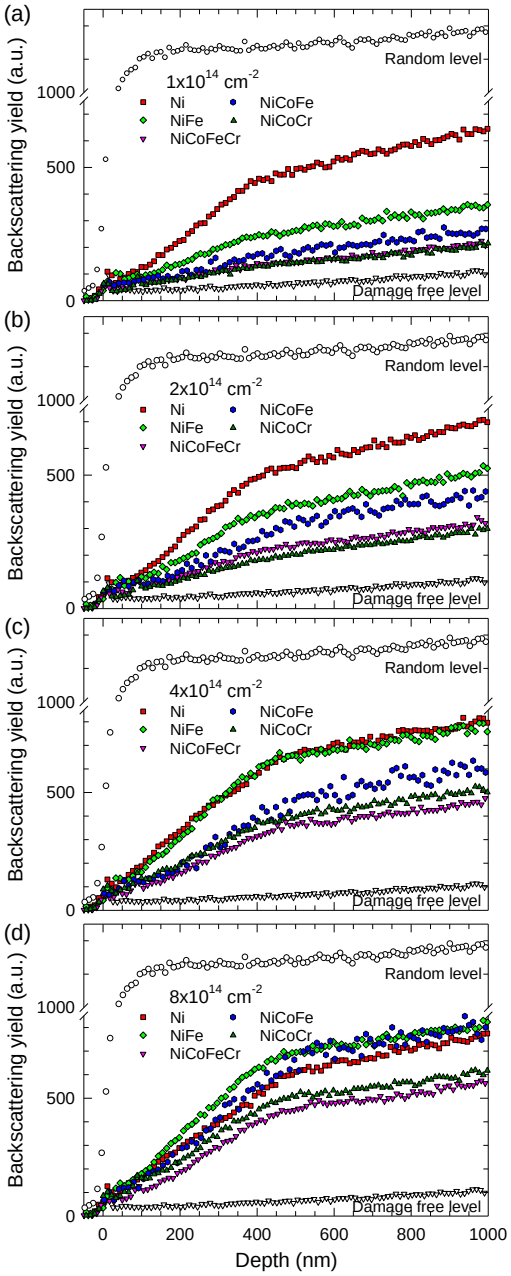

Fig. 8 Rutherford backscattering spectra along the (001) channeling direction. Different irradiation response in Ni and CSAs are observed under 1.5 MeV Ni irradiation at room temperature with fluences ranging from 1×10^{14} to 8×10^{14} cm^{-2}.

$Ni_{0.8}Fe_{0.2}$ is approximately 2.5 and 1.4 times lower than in Ni, respectively, due to efficient recombination in the compositionally disordered alloys. The difference in defect production between the alloys and Ni is governed by the diffusion of point defects during overlapping cascades [22]. Although the formation of a large interstitial cluster is observed in Ni and is attributed to the high mobility of Ni interstitials, only isolated point defects and small clusters are produced in $Ni_{0.8}Cr_{0.2}$. While the larger fraction of small defect clusters in the binaries is attributed to the higher migration barriers and slow kinetics, the direct evidence is yet to be seen experimentally. Independent studies of overlapping cascades in Ni, NiFe and NiCoCr [13] also report a reduction of damage after prolonged irradiation (**Fig. 7**) that agreed qualitatively with the experimental observations [2,12,13]. The results were explained in terms of the multi-elemental composition in NiFe and NiCoCr slowing down dislocation motion, leading to slower buildup of large damage structures. Simulated defect buildup in Ni and two equiatomic alloys (**Fig. 7**) suggests that initially the alloys show a slightly higher damaging rate, but on higher doses the alloys have much less damage than pure Ni, also in qualitative agreement with the experiments. The evolution of microstructure in concentrated alloys under irradiation should be qualitatively different from that in dilute alloys, due to the significantly modified point defect diffusion and defect cluster mobility resulting from local chemical environment.

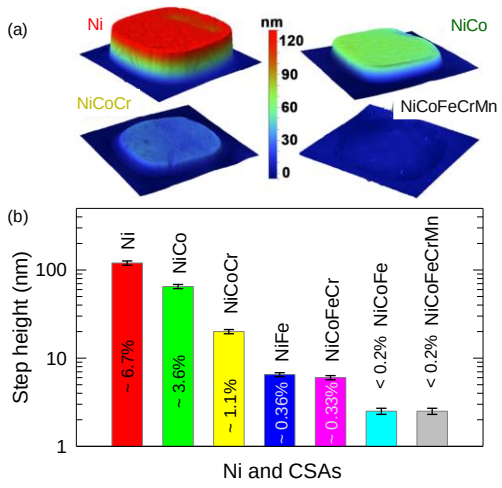

Fig. 9. Comparison of swelling between Ni and CSAs based on step height measurements. under 3 MeV Ni^+ irradiation to 5×10^{16} cm^{-2} at 500 °C. Adapted from Fig. 2 in Ref.17.

In order to investigate defect survival from multiple overlapping cascades at realistic fluxes, it is necessary to simulate defect evolution that occurs between the cascades. Accelerated aging approaches are establishing to describe such defect evolution after the initial picosecond timescale. Accelerated aging approaches based on calculating the barriers "on-the-fly" during a KMC run are being developed to describe defect evolution in the CSAs. The kinetic activation relaxation technique (k-ART) is an algorithm capable of simulating atomic systems over timescales reaching more than one second at RT, while accounting for off-lattice defects and elastic interactions [68]. To simulate the long-term aging of large disordered systems with cascade debris, this k-ART method has been recently modified [2,69], utilizing an active volume concept developed in an on-the-fly KMC [70], to describe significantly complicated system, such as CSAs. The original k-ART [68] can study systems containing up to a few thousand atoms, and the modified method [69] can efficiently simulate systems containing hundreds of thousands of atoms.

To understand effects of chemical complexity on defect evolution, recent successes in experimental work have provided crucial baseline information on improved irradiation response. Experimental evidence has demonstrated that defect dynamics can be modified by simply altering elemental species and composition of the CSAs. By changing from pure Ni metal to binary, ternary and quaternary alloys, a delayed accumulation can be achieved, as compared to Ni [2,12-14,17,23]. As shown in **Fig. 8,** different irradiation response is evident under 1.5 MeV Ni irradiation. The peak dose at depth of 375 nm is ~ 0.13, 0.27, 0.54, and 1.1 dpa for the ion fluence of 1, 2, 4 and 8×10^{14} cm^{-2}, respectively. At the relatively low doses (1×10^{14} cm^{-2} and 2×10^{14} cm^{-2}), significantly hindered damage accumulation is observed, as compared with pure Ni. As shown by the lower backscattering yield, NiCoCr and NiCrFeCo outperformed NiCoFe and NiFe. With increasing ion fluences to 4×10^{14} cm^{-2} and 8×10^{14} cm^{-2}, while the most radiation-resistant alloys are still NiCoCr and NiCrFeCo, different saturation level is observed, and irradiation-induced damage moves deeper into the samples (**Figs. 8c and 8d**). Specific alloying effects responsible for these observed responses are topics for further investigation.

4C. Microstructural evolution under prolonged high-temperature irradiation

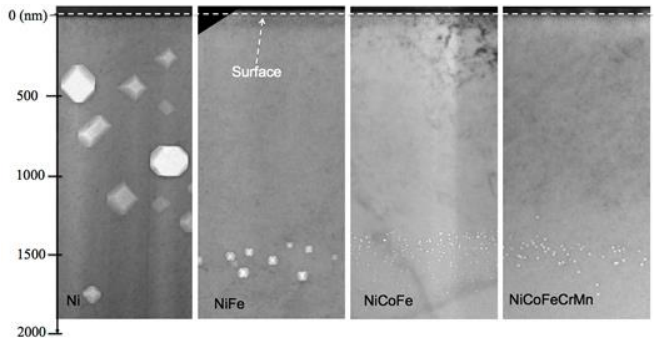

Fig. 10. Void formation in Ni and Ni alloys under 3 MeV Ni^+ irradiation to 5×10^{16} cm^{-2} at 500 °C. More complex alloys exhibit smaller void formation, reducing swelling.

A major challenge in characterizing defect clusters and understanding defect evolution is to establish links among microscopic models, defect observations at early stages, and mesoscale phenomena (interstitial loops and void swelling) under prolonged defect evolution. Enhanced irradiation resistance at high doses and high temperatures is essential for advanced reactor applications. Recent studies [14,17] have shown significant compositional impact on defect evolution under Ni ion irradiation at 500 ºC with a peak dose of ~ 53 dpa at a depth of ~ 900 nm. A dramatic reduction of swelling in complex alloys is shown in **Figs. 9** and **10**. TEM irradiation study in **Fig. 10** reveals a colossal difference in swelling behavior and defect cluster distribution. *In-situ* observation of defect migration and MD simulations indicate that 1D glide of interstitial loops occurs more readily in Ni than in the alloys. As compared to NiFe and other more complex CSAs, the relatively long 1D migration path observed in Ni leads to less recombination of interstitials and vacancies. On the other hand, the more localized defect motion in NiFe and other more complex alloys leads to the remarkably enhanced defect recombination and substantial reduction in void formation and volume swelling. The defect diffusion in CSAs depends on the properties and diffusion mechanisms of specific defects in their unique environment. The results here show that chemical complexity can be used to modify void and dislocation loop distribution.

5. Perspectives — Chemical Effects and Atomic-level Heterogeneity on Irradiation Performance

To design better materials for energy technologies, a thorough understanding of the underlying physics and chemistry of simple and complex solid solution systems is essential to identify, understand and ultimately control the non-equilibrium energy and mass transform processes in extreme radiation environments. The local atomic arrangement and the corresponding energy landscapes of materials can be modified, which is of course not limited to metals and alloys. These chemical effects may lead to remarkable differences in resistance to radiation damage or amorphization.

Oxides with similar structure can exhibit different damage and amorphization behavior [71,72-74]. In the study of radiation tolerance of complex oxides, pyrochlore compositions display distinctive responses to ion beam-induced amorphization, depending on the chemical composition [72,75]. Pyrochlore materials, in the $A_2B_2O_7$ crystal structure, have remarkable elemental versatility. These changes in structure and chemical durability affect long-term performance of the actinide waste forms. Radiation studies of actinide-doped, synthesized or natural pyrochlores indicate that pyrochlores with Ti, Nb, and Ta as the major B-site cations become amorphous as a result of the gradual accumulation of cascade damage. With the increasing ionic radius of the A-site cation, from Lu^{3+} (0.098 nm) to Gd^{3+} (0.106 nm), the critical temperature for amorphization, above which the material will not be amorphized, increases from 480 K (for $Lu_2Ti_2O_7$) to 1120 K (for $Gd_2Ti_2O_7$) [76,77] under Kr^+ ion irradiation; however, the critical temperature for this material is nearly constant (1000 K) under heavy ion irradiation [78]. Zirconate pyrochlores are generally resistant to radiation-induced amorphization, and both $Gd_2Zr_2O_7$ and $Er_2Zr_2O_7$ remain crystalline at doses as high as 100 dpa at cryogenic temperatures [71,79]. Sickafus et al. [71] point out that fluorite crystal structure should accept radiation-induced defects into their lattices far more readily than a structurally similar pyrochlore crystal structure, therefore, fluorites are inherently more radiation resistant than pyrochlores. Sickafus et al. [71] have, however, proposed that complex oxides, which possess both complex chemistry and structure and therefore an inherent propensity to

accommodate lattice disorder, should be able to resist lattice instability in the presence of a displacive radiation environment.

In contrast to Sickafus' hypothesis, Trachenko et al. [73] have suggested that the type of interatomic force may hold the key to radiation performance. He proposes that the ability to form a short-range covalent network leads to damage stabilization and makes a material amorphizable by radiation damage. The long-range high ionicity, on the other hand, results in higher resistance. Such argument may be supported by the fact that most metals and alloys where metallic bonding has even longer range are in general radiation resistance. Examples supporting his argument in oxides include SiO_2, TiO_2, and GeO_2. Crystalline SiO_2 is easily amorphizable but TiO_2 is more resistant than SiO_2 and GeO_2, which is attributed to its larger iconicity in the bonding of TiO_2 than in the classical network formers SiO_2 and GeO_2. Trachenko has further demonstrated that complex titanates (such as perovskites $CaTiO_3$, $SrTiO_3$, $BaTiO_3$, pyrochlores $Gd_2Ti_2O_7$, $Sm_2Ti_2O_7$, $Eu_2Ti_2O_7$, $Y_2Ti_2O_7$, zirconolite $CaZrTi_2O_7$), due to disordered covalent Ti-O-Ti, are readily amorphizable by radiation damage. On the other hand, the binary oxides MgO, ZrO_2 and Al_2O_3 are known to be highly resistant to amorphization by radiation damage, which Trachenko attributes the performance to the high ionicity of these binary oxides [73]. The same argument, high ionicity of Zr-O bond, is used to explain the extreme resistance of zirconate oxides $Gd_2Zr_2O_7$, $Sm_2Zr_2O_7$, $Nd_2Zr_2O_7$, $Ce_2Zr_2O_7$ and $Er_2Zr_2O_7$. Trachenko further proposes that the resistance to amorphization of a complex (non-metallic) material is defined by the competition between the short-range covalent and long-range ionic forces.

Another well-studied case of chemical complexity effects on radiation damage involves III-V semiconductors. Due to their importance in optoelectronics, radiation damage in III-V semiconductors have been studied extensively [80-84]. The case of $Al_xGa_{1-x}As$ compounds is particularly intriguing, in that it shows a drastic change in damaging behavior when only a small fraction of Al is used to replace Ga. [85]. This is particularly surprising since during the addition of Al, the crystal structure remains the same, and there are no drastic changes in lattice constant, band gap or any other basic materials property. The sensitivity has been suggested to be related to higher defect mobility in AlAs [83], however, why the effect occurs already at low Al concentrations has not been explained.

Chemical effects on resistance to amorphization are thus still an open research topic. Chemical complexity can induce atomic-level stress that is not limited to only crystalline materials. Nearly 30 years ago, well before the development of the HEAs, the concept of atomic-level stresses related to local incompatibilities was argued as a general means for describing complex atomic structures [86]. The authors state that only in perfect crystals in which all the atoms are equivalent, such incompatibilities do not exist. Local incompatibilities are, however, present in ordered structures with non-equivalent atoms, such as in CSAs [2], and in any disordered structure, such as in BMGs [87,88]. Egami in 2010 pointed out [88] that major mysteries still remain in the behavior of glasses and liquids at the atomic level, and identifying the microscopic mechanisms that control the properties of glasses is one of the most challenging unsolved problems in physical sciences. He further stated that as metallic glasses are atomic glasses with relatively simple structure, they may offer better opportunities to advance our fundamental understanding on the nature of the glass transition. Recent studies investigate the variations of inherent structures and properties with respected to the hopping between different local minimum states on a potential energy landscape (PEL) in metallic glasses [89,90], a material system with a complex energy landscape similar to CSAs. From the perspective of PEL, the authors demonstrate that the activation energy spectra consistently change at varying thermal environments, and PEL structures are closely linked to energy dissipation where a higher density of local minima in PEL is more likely to trigger cascade relaxations and thus may affect the primary damage production. Evaluation of potential energy differences between initial minimum states and nearby saddle states on PEL with different local structure (atomic arrangements) reveals that the susceptible atoms involved in deformation of metallic glasses can be characterized by the correlations between atomic displacements and atomic stress changes.

The similarity of atomic-level chemical complexity and site-to-site inhomogeneity (lattice distortion), yet on a relatively simple structure is the common characteristic in complex oxides, III-V semiconductors, MBGs and CSAs. In CSAs, different from traditional alloys, the intrinsic lattice

distortions, the intricate electron-electron interactions [2,12], the complex energy landscapes, and local stress fluctuations are shown to have profound effects on the mechanical properties [3-11], yet the research effort to clarify links between these intrinsic variables and microstructural evolutions under non-equilibrium radiation condition is just starting. Given the complexities of lattice distortion and atomic stress fluctuation, the defects in CSAs are sitting in a wide range of distributions of local environments, in contrast to the very explicit and narrow distributions in traditional alloys. It therefore makes the study of microstructural evolutions in CSAs particularly challenging.

Effect of extreme chemical complexity on defect dynamics and radiation performance in concentrated solid-solution alloys is an exciting field to explore. Given that relatively little is known of extreme chemical effects on defect dynamics under thermal equilibrium condition, and even less known about their impact in a high radiation environment that is far away from non-equilibrium condition, the pioneering work on the *effects of chemical complexity on defect dynamics and radiation performance in metals and alloys reviewed* in Section 3 and 4 is highly intriguing. There are many open questions, including (1) how can we understand the intricate correlations of the atomic or electronic constituents in CSAs? (2) how do the electronic and atomic subsystems respond to energy deposition separately and collectively, and how can we control energy flow and mass transport during the correlated, non-adiabatic electronic and atomic processes? (3) how do we understand, predict, and ultimately control the dynamics of excited or non-equilibrium states, and to control matter away – especially very far away – from equilibrium? and (4) how can we reveal underlying crucial knowledge for the development of transformative materials with optimized functionality in extreme conditions.

The scientific challenges include (1) assessment of static structure in CSAs in terms of short- and long-range elemental disorder, local stresses, lattice distortions, etc, and examination of how these variable would influence the energy dissipation mechanisms (2) description of the complex energy landscapes in CSAs, especially the temperature-dependent energy landscapes, as the changes of thermal environments may lead to atoms rearrangements and also considerably modify energy dissipation as well as the mass transport processes over a wide range of time and length scales; (3) exploration of early stages of radiation damage beyond the current empirical description; and (4) prediction of the microstructural evolution from the fundamental correlations between atomic level stress fluctuation and lattice distortion (atomic displacement from ideal lattice site). The scientific understanding on diffusion in these alloys will, for example, shed light on how to model diffusion in complex multi-component semiconductor alloys that are increasingly being employed in new electronic devices. More importantly, the knowledge may eventually reveal a unified description of chemical effects on irradiation performance in solids (metals, alloys, metallic glasses, semiconductors, and insulators, etc).

6. Summary

Alloy development or innovation with much improved radiation resistance performance demands taking advantage of property enhancements that go beyond linear extrapolation. A clear demonstration of enhanced radiation resistance is reported by tailoring chemical disorder from pure Ni to binary and more complex solid solutions. Recent research has revealed that changes in chemical complexity have substantial influence on defect dynamic and damage accumulation in CSAs. Experimental and modeling results in solid-solution alloys with various compositional complexities (binary, ternary, quaternary, and quinary HEA solid solutions) have shown that defect production and subsequent recombination can be modified. Systematically understanding of how material properties can be tailored by chemical complexity and their influence on defect dynamics may pave the way for material by design at the level of atoms and electrons, may inspire new design principles of radiation-tolerant structural alloys for advanced energy systems and for new defect engineering paradigms benefiting broader science and technology.

While this review focuses on the intrinsic properties of concentrated solid-solution alloys, advancement in nanotechnology should not be overlooked. Studies worldwide have shown that nano-scale features can significantly affect defect dynamics and microstructural evolution [91,92]. Some nanomaterials have shown to have high radiation tolerance including nanostructured crystalline materials, such as Fe-based or Ni-based ODS alloys. Taking advantage of the existing knowledge from

nanotechnology, new knowledge from controlling chemical complexity together with the advances achieved from incorporation of nano-scale features (e.g. low level of substitutional additions, nanoparticles, grain boundaries, etc) in concentrated solid-solution alloys may lead to additional alloy design criteria to meet various application requirements. While the work reviewed here is more closely related to radiation effects, understanding the response of materials to energy deposition from unique aspects of defect evolution is fundamentally important and can have broad interests that is not only limited to advanced alloy design. The breakthrough in this open field will lead to science-based rational accelerated material discovery and radical changes in the field of radiation effects that is not limited to structural alloys.

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