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Viewpoint

How Does Short-Range Order Impact Defect Kinetics in Irradiated Multiprincipal Element Alloys?

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The effect of high-energy particle irradiation on materials is often detrimental, yet it can be beneficial as in orienting high-density magnetic alloys by promoting chemical order.[1] Radiation-induced ordering postulated and proved by Averbach more than half a century ago[2] has been observed frequently in binary alloys.[3] Multiprincipal element alloys (MPEAs), including medium- and high-entropy alloys that comprise multiple principal elements in high concentration, are presumed to be solid solutions corresponding to maximum configurational entropy. The ideal random mixing in MPEAs, however, may only be possible at high temperatures.[4] As the temperature decreases, enthalpic contribution to the total free energy may become predominant and induce local ordering of the chemistry. Indeed, appreciable short-range order has emerged in long-time annealed MPEAs,[5] and the degree of ordering is further enhanced after irradiation[6,7] (Figure 1). The development of chemical short-range order, whether from material processing or irradiation, could largely alter the kinetic behavior of defects created by radiation damage in these materials. For example, nanometer-sized dislocation loops,[8] which exhibit one-dimensional (1D) fast diffusion in pure metals or alloys, do not occur in CrCoNi, CrFeCoNiMn, and CrFeCoNiPd,[9,10] the medium- and high-entropy alloys having been shown to possess short-range order.[5,11] This suggests that the local chemical order, intentionally engineered into the materials or in situ precipitated under irradiation, will influence defect behavior and radiation response of MPEAs. This Viewpoint is intended to discuss hypothetical perspectives on the role of local chemical order in defect kinetics in irradiated MPEAs and to stimulate discussion and new strategies for controlling radiation defects migration and annihilation through tailoring the ordering at the nanometer scale.

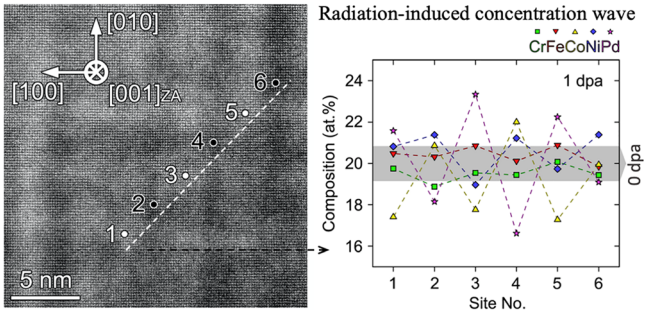

Figure 1. Short-range ordering induced by irradiation. The concentration wave suggests local chemical ordering or clustering in CrFeCoNiPd alloy irradiated to 1 dpa (displacements per atom). Reproduced with permission from ref 7. Copyright 2017 Elsevier Inc.

Here, the potential effects of short-range order on the kinetics of three major types of defect, including point defects, defect clusters, and grain boundaries, are speculated, and specific mechanistic hypotheses pertaining to the role of local ordering are conceived.

ROLE OF LOCAL CHEMICAL ORDER IN POINT DEFECTS DIFFUSION

Displacement cascades, involving a chain of atomic collisions induced by an energetic particle, produce interstitials and vacancies (Frenkel pairs) and clusters of these defects. The diffusion of individual interstitials and vacancies, governing defect recombination and nucleation and growth of defect clusters is enabled by elementary defect jumps from one stable position to another. Both the jump frequencies and directions of a point defect are nonequal in multicomponent systems because of the diversity of local chemistry surrounding it. For example, vacancies migrate through jumps to the nearest neighboring sites; in single-component (pure) systems, all the migration pathways and the associated jump rates (i.e., migration energy barriers) are equivalent, implying a random walk of defects. For multicomponent alloys, however, the vacancy migration rates and energy barriers, depending on the local atomic environment, become nonequivalent and less uniform (diffusion heterogeneity), originated from the rugged potential energy landscape.[12] If local chemical order appears in the system, it is reasonable to expect that the heterodiffusion of vacancy will be further intensified.

The interstitial diffusion mechanism involves rearranging a dumbbell configuration—the stable interstitial structure in which two atoms are symmetrically split about a vacant lattice site. In pure bcc iron, the migration begins with the energetically favorable ⟨110⟩ dumbbell interstitial, which rotates and aligns in the ⟨111⟩ direction, followed by the formation of the ⟨111⟩

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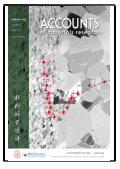

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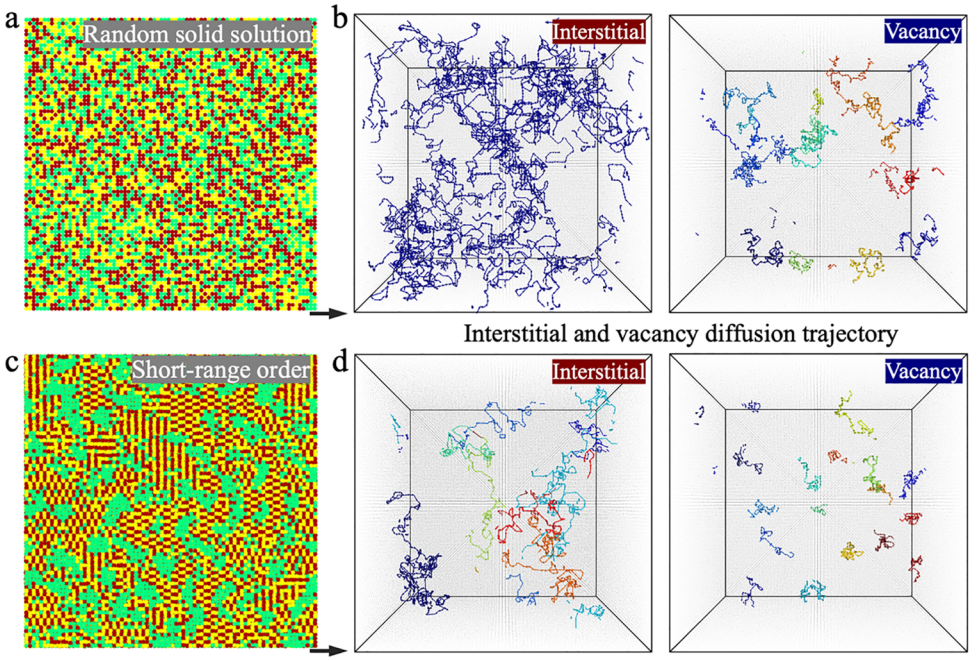

Figure 2. Short-range order traps point defects, reducing their diffusivity. Interstitial and vacancy diffusion trajectories in (a, b) a random solid solution of CrCoNi and (c, d) thermally annealed CrCoNi with chemical short-range order.

crowdion (saddle point) and then relaxation to a new dumbbell interstitial (Johnson mechanism[13]). In MPEAs the conceivable lattice distortion can make the interstitial migration through the crowdion saddle position difficult. Short-range order would also render an interstitial jump energetically unfavorable as it would interrupt local chemistry. It is therefore hypothesized that increasing the degree of local ordering, which roughens the underlying potential energy landscape of vacancy and interstitial diffusion, raises defect migration barriers and enhances point defect diffusion heterogeneity (less randomness). In Figure 2, we demonstrate the role of short-range order in point defects diffusion by showing interstitial and vacancy diffusion trajectories in fast quenched (random solid solution) and annealed (with local chemical order) CoCrNi alloys, where the introduced local chemical order limits and localizes defects diffusion.

EFFECTS OF LOCAL CHEMICAL ORDER ON THE BEHAVIORS OF DEFECT CLUSTERS (DISLOCATION LOOP AND VACANCY CLUSTER)

Condensation of interstitials or vacancies forms dislocation loops bounding a platelet of these defects. Dislocation loops resulting from defects agglomeration can be sessile or glissile, depending on their Burgers vector. Faulted Frank loops, regardless of interstitial or vacancy-type, are sessile and can only move through a climb. Perfect dislocation loops, however, are glissile, as they can undergo a glide motion along the direction of the Burgers vector. In both bcc[14] and fcc[15] metals, nanometer-sized dislocation loops with a perfect Burgers vector exhibit fast 1D glide diffusion in the absence of stress. The mobility of dislocation loops, depending on composition, is considerably reduced in alloys.[16] Interestingly, the 1D loop motion becomes rather scarce or does not occur in MPEAs such as CrCoNi, CrFeCoNiMn, and CrFeCoNiPd.[9,10] The vanishing of loop motion may pertain to radiated-induced chemical redistribution and local ordering in the vicinity of dislocation loops or in the matrix of the materials. For example, the interstitial-type dislocation loops, favoring small atoms, result in inhomogeneous element concentrations (atom segregation or depletion), and the locally biased element distribution akin to the Cottrell atmosphere limits dislocation mobility by raising its migration energy barrier. Short-range order formed in the matrix should also impede dislocation loop motion. The slip plane of dislocation loops is a cylinder surface with the axis perpendicular to the loop plane (i.e., along Burgers vector direction). The glide motion, inducing slip displacement of atomic planes above or below the loop, destroys the local ordering of chemistry associated with the slip plane and creates an antiphase boundary (swept area in Figure 3a). The disruption of local order incurs an energy penalty, rendering the 1D loop diffusion energetically unfavorable. Especially for low stacking fault energy fcc alloys, a perfect dislocation tends to dissociate into two partials outlining stacking fault (i.e., extended dislocation), and this dissociated dislocation configuration further reduces its mobility.

Unlike interstitial clusters, which predominantly have stable disc-shaped configuration, vacancy clusters possess various possible structures, manifesting as a perfect loop, faulted Frank loop, void, or stacking fault tetrahedron (SFT), regulated by their formation energies. Stable SFTs, resulting from the self-organization of vacancy cluster or the transformation of vacancy-type Frank loop, are prevailing in low stacking fault energy materials subjected to irradiation. Since local chemical order raises the stacking fault energy and increases its spatial variation,[17] we speculate that the formation of stable SFTs is hindered in MPEAs.

INFLUENCE OF LOCAL CHEMICAL ORDER ON RADIATION-INDUCED GRAIN BOUNDARY MIGRATION

Grain boundary or interface acting as radiation defect sink inevitably undergoes migration under irradiation, ultimately leading to radiation-induced grain growth. The driving forces responsible for boundary motion come from various sources such as a gradient of defect density and capillary pressure of

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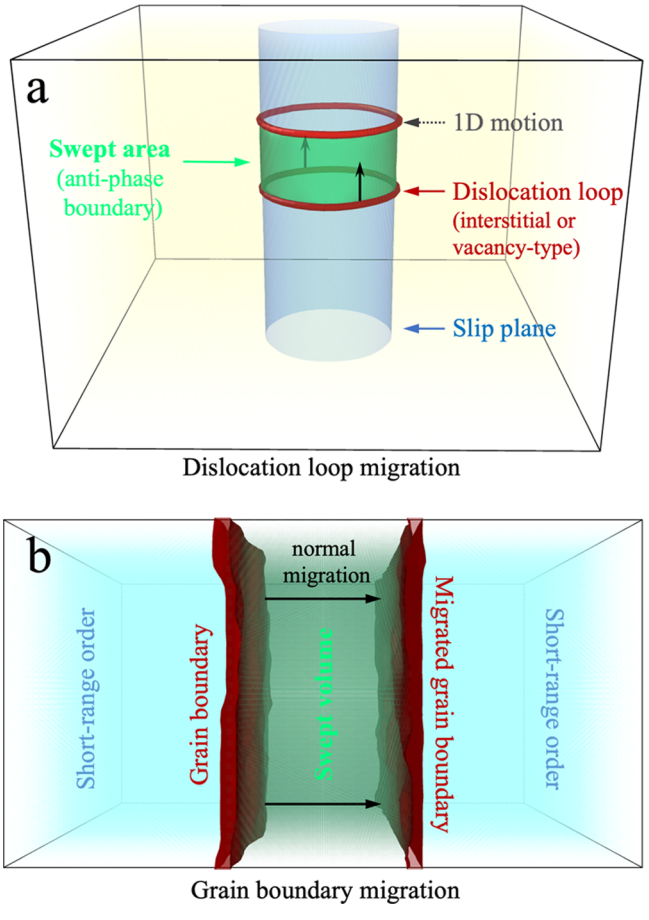

Figure 3. (a) Schematic illustration of 1D glide motion of a perfect dislocation loop with a Burgers vector perpendicular to the loop plane. The loop glide breaks local chemical order associated with the slip plane and creates an antiphase boundary (swept area). The disruption of local order incurs energy penalty, rendering the 1D glide motion energetically unfavorable. (b) Grain boundary migration alters the crystallographic orientation of the matrix and interrupts the ordering in the swept volume. It is hypothesized that chemical short-range order reduces the grain boundary migration rate by lowering the thermodynamic driving force and grain boundary mobility.

curved boundary. We hypothesize that if local chemical order is engineered into the grain matrix, the thermodynamic driving force for boundary motion will be lowered. The locally ordered clusters, analogous to coherent nanoprecipitates, will exert a drag force on a grain boundary, reducing the driving force for boundary migration. For example, when a grain boundary sweeps its grain matrix, the local chemical order corresponding to low free energy will be destroyed because grain boundary migration alters the crystallographic orientation of the swept matrix (Figure 3b). Therefore, the interruption of local order caused by grain boundary migration increases the free energy and lowers the grain boundary migration rate. Besides the thermodynamic driving force, local clusters interacting with the grain boundary could raise the boundary migration energy barrier and decrease its mobility. Through these mechanisms, the grain boundary migration rate can be considerately lowered by the introduction of short-range order, as it thermodynamically and kinetically impacts grain boundary migration behaviors.

Interfaces, grain boundaries, and secondary phase dispersoids, which are the venues for radiation defect recombination and annihilation, are often engineered into materials to improve their radiation resistance. It is worth noting that properties and features associated with these defect sinks are not static but evolving under irradiation (for instance, the mobility of a grain boundary can increase by a factor of 10 after irradiation[18]). Broadly, the 0D local chemical order or 1D tangles of nanowires[19] may stabilize or serve as the defect sinks and maintain robust mechanical and chemical integrity of the materials under extreme environments.

CONCLUDING THOUGHTS

As an emerging class of materials, MPEAs have attracted increasing attention owing to their extraordinary properties, including diminished radiation defects, enhanced swelling resistance, and suppressed solute segregation when compared to traditional solid solutions. While the fundamental atomic mechanisms and their correlation to the improved radiation performance remain to be elucidated, the local chemical order may be the salient feature that makes MPEAs distinct from traditional alloys. By analyzing the experimental and theoretical data, we speculate that the hidden short-range order plays a vital role in radiation defect dynamics and kinetics, contributing to improved radiation tolerance. From this viewpoint, motivating questions regarding short-range order arise: (i) how does the local chemical order influence defect migration, coalescence, and growth, (ii) what are the new atomistic mechanisms and processes enabled by local order, which leads to radiation damage reduction, and (iii) is tuning the degree of local ordering able to promote defect recombination and to alleviate radiation-induced degradation? Answering these questions, which requires simulations and experiments tailored to isolate the fundamental mechanisms, will facilitate the material design and synthesis strategies to manipulate defect behavior via engineering nanoscale features, giving rise to tunable material properties.

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Notes

The author declares no competing financial interest.

Biography

Penghui Cao is an Assistant Professor in the Mechanical and Aerospace Engineering and Department of Materials Science and Engineering at University of California Irvine since January 2019. Before this, he was a postdoctoral associate at Massachusetts Institute of Technology after obtaining his doctorate from Boston University. His research involves developing microscopic modeling algorithms to probe the fundamental mechanisms governing deformation behaviors and responses of materials under extreme environments.

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