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On the possibility of universal interstitial emission induced annihilation in metallic nanostructures

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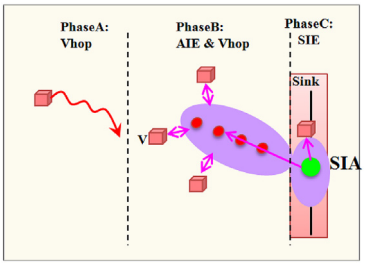
GRAPHICAL ABSTRACT



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ABSTRACT

Nano-structured metals have been explored as self-healing materials for radiation damage due to vacancy-interstitial recombination at interfaces, such as grain boundaries (GBs) in nanocrystals (NCs) and free surfaces in nanoporous metals (NPs). The annihilation in copper was recently proposed to be via the interstitial-emission (IE) from the GB. However, whether the IE is applied as a possibly universal mechanism in other NPs and NCs deserves further investigation. The interstitial is often considered to overcome a large binding energy with the GB/surface to migrate out of the GB/surface and induce annihilation. In this work, with emphasis on the IE in tungsten where the interstitial is exceptionally tightly bound to the tungsten GB/surface, we found that the interstitial only needed to migrate over a small distance from the GB/surface to recombine with the vacancy nearby at a small energy barrier. During the process, the annihilation region around a static interstitial at the GB/surface propagated or extended greatly to the adjacent bulk area. The annihilation was found to be via the IE from the GB/surface or coupled vacancy hop with the IE. The ratio of the interstitial-GB/surface binding energy to the trapping-radius of the GB/surface for the interstitial was proposed to be a better qualitative indicator for the difficulty in the IE than the binding energy. Given that the IE works in the investigated NPs and NCs tungsten, iron and copper where the interstitials of distinct configurations bind with the GBs/surfaces at diverse levels, the IE mechanism may work universally in various nano-structured metals.

1. Introduction

Metals such as stainless steels with iron (Fe) as a matrix and tungsten (W) are widely used as the core structure components of

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fission and fusion reactors [1,2]. Under operation conditions, Fe and W will be heavily exposed to the radiation of neutrons, protons or heavy ions. Consequently, a large number of defects are produced, including point defects and defect clusters, such as self-interstitial atoms (SIAs), vacancies (Vs), voids, and SIA-loops [3–9]. These defects significantly degrade the mechanical properties of metallic materials in terms of radiation hardening, embrittlement and irradiation-induced creep [10–13]. It is thus of engineering importance to design and find novel nuclear materials that can sustain large amounts of damage [14–16].

The ability of a material to resist radiation damage is determined by how well the microstructure can remove SIAs and Vs in equal numbers. In recent years, interfaces such as grain boundaries (GBs) in nano-crystalline materials (NCs) [3–9,17,18] and free surfaces in nano-porous metals (NPs) [19–21] have been demonstrated to well alleviate radiation damage. Ultra-fine-grained W shows resistance to irradiation embrittlement and/or recrystallization embrittlement [6,7], even at a low temperature of 563 K [7] where bulk Vs are actually immobile. NPs with a large surface-to-volume ratio have the potential to be extremely radiation tolerant.

The improved radiation performance of the NCs and NPs could be attributed to the GB/surface promoted V–SIA annihilation. However, the annihilation kinetics and atomic process are not well understood. In 2010, Bai et al. [22] reported an interstitial-emission (IE) induced annihilation mechanism for healing radiation damage near face-centered cubic copper (Cu) GBs. They showed that the Cu GBs have a surprising "loading-unloading" effect. Upon irradiation, SIAs were firstly loaded into the GB, which then acts as a source, emitting SIAs to annihilate Vs near the GB. Nevertheless, it is not clear whether the IE-induced annihilation mechanism could be applied as a universal mechanism in other metals where the GBs/surfaces bind SIAs with different levels of the sink strength (the binding energy of the SIA with the GB/surface).

There are controversies regarding both the kinetic condition and the atomic detail of the mechanism [23–31]. On the one hand, some researchers tend to believe the IE mechanism works in body-centered cubic (bcc) Fe due to a comparable value of the SIA-GB binding energy in Fe (2.7 eV) to that in Cu (1.6 eV). In 2013, using classical molecular dynamics (MD), Chen et al. [23] found that the V-SIA annihilation at the GB in Fe involved the movement of chain-like group defects. In 2016, by using the auto-basin-climbing (ABC) method [24], Tang et al. found connections between the defect-GB interactions in the Cu GB [22] and that in the Fe GB [23]. They attributed the discrepancy in geometric descriptions of these two GB-induced recombination mechanisms to the different lattice structures (fcc in Cu, bcc in Fe).

On the other hand, some researchers tend to consider that the IE mechanism fails to work in the system where the GB sink strength for the SIA is extremely high, e.g. in nano-crystallines W and molybdenum (Mo). Based on MS calculation [27], Li et al. found that the W SIA-GB binding energy is as high as 7.5 eV [27], leading to the modification in the annihilation mechanism near the GB in W. The monitoring of atomic movements indicated a collective motion of multiple atoms during the annihilation of the SIA–V near the GB. Borovikov et al. [31] also found that the energy of the $\sum$5(0 1 3)/[1 0 0] GB with a SIA in the bulk is about 7 eV higher than the energy of the system with a SIA at the GB. Their estimation of the transition time suggested that the escape time for the SIA from the GB at the system temperature of $T = 1000$ K is about 10^{22} s, and even at $T = 1500$ K is about 10^{10} s. Thus, apart from the possibility of direct annihilation with a nearby V, as has been observed in Cu [22], they did not expect the SIAs, once bound, to escape from the GBs in W.

To show whether the IE-induced annihilation works universally at the GB/surface in metals, we revisited this mechanism in NCs and NPs W, Fe and Cu by using the MS method with emphasis on W. MS calculations of the kinetics for the IE-induced annihilation near the GB/surface in W, Fe and Cu suggested that the annihilation region around a static SIA at the GB/surface propagated or extended towards the region in the vicinity of the sink after the SIA migrated over a small distance from the GB/surface. Consequently, the V around the annihilation region was recombined with the SIA at a low energy barrier via the direct IE or coupling of the V-hop with the IE. The IE-induced annihilation may work universally at the GB/surface in various metals.

The article was organized as follows: in the results section, we begin with calculating the SIA binding energy with the GB/surface in W, Fe and Cu. Then, we discussed the annihilation mechanism within the spontaneous annihilation region (SAR). We further investigated the annihilation kinetics and atomic picture for the annihilation of the V out of the SAR. We then explored the dynamic relation of the annihilation with the IE. Finally, we proposed that the ratio of the SIA-GB/surface binding energy to the trapping-radius of the GB/surface for the SIA may be a better qualitative indicator for the difficulty in the IE than the binding energy.

2. Computational method

2.1. GB and surface models and atomic potential

Metals W, Fe and Cu were chosen as three typical model systems with different lattice structures of bcc W and Fe, fcc Cu and distinct SIA configurations of <1 1 1> crowdion in W, and <1 1 0> dumbbell in Fe, <1 0 0> dumbbell in Cu, respectively. Different levels of SIA-GB binding energies in these systems act as another factor for choosing the model systems, as revealed in some GBs and surfaces in these systems [22–31]. The GB studied in this work is a $\sum$5(3 1 0)/[0 0 1] symmetric tilt GB in bcc W and Fe. For fcc Cu, a $\sum$11(1 1 3)/[1 $\bar{1}$ 0] symmetric tilt GB was used. The two GBs have been frequently modeled in studying radiation effects [22–31]. To explore the generality of the simulation results, a total of 46 GBs in W were also modeled by using a different interatomic potential. The detailed structural parameters are given in Table 1 in Ref. [32]. These GBs have distinct periodical structural units along the GB with various lengths.

The creation and relaxation procedures are refereed to Ref. [22]. Periodic boundary conditions were applied in the three directions of the GB systems. The GB energy was minimized through the rigid-body translations of one grain relative to the other in the two directions parallel to the GB, followed by atomic relaxation in all the three Cartesian directions at 0 K. Assuming the length of the minimal periodical structural units in the two directions parallel to the GB plane is *px* and *py*, respectively, and the corresponding translation step is *stepx* and *stepy*, one has to perform $Nx \times Ny$ ($Nx = px/stepx$, $Ny = py/stepy$) structural relaxations. Although a small step leads to a high resolution of the potential energy variation surface as a function of the translation vector, as shown in Fig. 1 in Ref. [32] for the *stepx* and *stepy* of 0.1 Å, more time is consuming. In most of the GB structural relaxation, a value of 0.5 Å was employed for both stepx and stepy. The energy variation surfaces are shown in Figs. 2–4 in Ref. [32]. The relaxed structures for the three GBs in W, Fe and Cu are shown in Fig. 1(a)–(c).

Low-index surfaces (1 0 0) and (1 1 0) were built. Fig. 1(d)–(f) shows the relaxed structures for surface (1 0 0). The model size has been checked to be large enough to avoid the interaction of a defect with the free surface in the direction normal to the GB plane, and the interaction of the defect with the other free surface in the surface model.

Both the bond-order potential (BOP) that includes three-body contributions and angular dependence [33] and the embedded-atom method (EAM) [34] were used for investigating the V-SIA