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Radiation resistance of nano-crystalline iron: Coupling of the fundamental segregation process and the annihilation of interstitials and vacancies near the grain boundaries

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ABSTRACT

Finding novel nuclear materials with high radiation resistance is very important for the nuclear industry and requires the understanding of the self-healing of radiation damage in such novel materials as nano-crystalline iron. Combining molecular dynamics simulations, molecular statics calculations and the object kinetic Monte Carlo method, we found that the self-healing capability of nano-crystalline iron is closely related to the coupling of the individual fundamental segregation and annihilation processes of vacancies and interstitials near the grain boundary (GB). Statically, both near the GB and at the GB, a low-energy-barrier/barrier-free region forms around the interstitial which promotes the annihilation of vacancies. The annihilation process was found to always involve the collective motion of multiple atoms due to the recovery of the strained atoms around the interstitial. Dynamically, the annihilation involves two coupled processes. Before segregating into the GB, the interstitial annihilates lots of vacancies near the GB as it diffuses near the GB together with the low-barrier region. In addition, although the interstitial is tightly bound to the GB after segregation, it efficiently removes the vacancies near the GB while moving along the GB, with the low-barrier region extending into the neighborhood of the GB and even into the grain interior. These two mechanisms were found to work at low temperatures, even temperatures where the vacancy was immobile. This study revealed the interaction of the major radiation defects at different scales and thereby uncovered the origin of the high radiation resistance of nano-crystalline iron.

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1. Introduction

Grain boundaries (GBs), the interfaces between grains, strongly determine the performance and properties of devices in many different fields, e.g., by affecting a material's mass transport properties [1,2], strength, and deformation behavior [3–5]. In the field of nuclear energy, GBs were observed to significantly affect the radiation resistance of nano-crystalline materials with grain sizes smaller than the grain sizes of common poly-crystalline materials [6–9]. Methods for improving the radiation resistance of crystals by reducing the grain size have been studied for almost four decades [10]. Recently, it has been demonstrated that a reduction of the grain size can significantly reduce the accumulation of radiation defects in nano-crystalline metals [11–16], alloys [17,18] and oxides [19,20]. Often, the radiation tolerance of nano-crystalline metals strongly depends on fundamental processes in such systems, i.e., the diffusion, segregation and annihilation of self-interstitial atoms (SIAs) and vacancies (Vs) near the GBs. These processes can be used to define the role of GBs in modifying the behavior of SIAs and Vs

near the GBs.

It is well-known that defects tend to aggregate at GBs [1,2]. The segregation of small amounts of solute atoms can significantly change the fracture toughness and corrosion resistance of metallic alloys by several orders of magnitude leading to, for instance, the well-known effect of hydrogen embrittlement and stress corrosion cracking. Irradiation-induced defects, SIAs and Vs, are expected to be efficiently trapped by GBs, which explains the enhanced radiation resistance of nano-crystalline materials [21–32]. Molecular statics (MS) simulations at 0 K implied that it is thermodynamically favorable for SIAs and Vs to aggregate at the GBs [25–27,29,30]. Extensive energetic calculations of the segregation of SIAs and Vs in α-iron were performed by Tschopp et al., and their results suggested that a GB provides a larger energetic driving force for SIAs to segregate to the GB than for Vs [27]. Similar results were obtained for the segregation of SIAs and Vs in copper, tungsten and molybdenum [25,29,30]. Meanwhile, on the atomic scale, SIAs have been often observed to move towards the GBs in molecular dynamics (MD) simulations of primary radiation damage near GBs, whereas the Vs were generally observed to be immobile at the nanosecond time scale of the MD simulations [21–26,28,29,31,32]. Considering that GBs act as defect sinks, Singh and Foreman proposed that the void density in austenitic stainless steel grains depends on the grain size [33]. Their rate-theory calculations indicated that the depletion of Vs due to grain boundary trapping suppresses void formation. This is supported by the results of our object kinetic Monte Carlo (OKMC) calculations (see Figs. 1 and 2 in Ref. [34] which were obtained by only incorporating the segregation of point SIAs and Vs into the model). An improved radiation resistance was observed for fine-grained tungsten even at a low temperature of 563 K [15]. At this temperature, the V in the grain was found to actually be immobile. Such an improved radiation tolerance was also observed for gold at low temperatures [12]. Under these conditions, the GB can no longer absorb bulk Vs, implying that the described role of a GB as defect sink cannot explain these experimental results. The interaction between defects and GBs may therefore be far more complicated than previously considered.

In this study, we focus on the role of the GB as a catalyst for the V–SIA annihilation, which has been proposed to enhance the radiation tolerance of nano-crystals [25,29]. Recently, after studying a single-element model for copper with a face-centered cubic structure, Bai et al. observed a surprising phenomenon that the interstitial-loaded GB acted as an interstitial source, emitting interstitials via a replacement process along ⟨1 1 0⟩, with chains of up to five atoms pushing from the GB to anneal vacancies in the bulk, each atom moving about one nearest neighbor distance [25]. They referred to this mechanism as "interstitial emission" (IE) which was expected to efficiently anneal radiation damage in nano-crystalline copper due to a low annihilation energy barrier. However, the generality of this IE mechanism for other metallic systems has not been assessed, which may depend on the GB sink strength, i.e., the binding energy for the binding of the defect to the GB or the segregation energy. Quite recently, we have examined the V–SIA annihilation mechanism in tungsten where the SIAs were tightly bound to the GB due to an exceptionally large binding energy of about 7.5 eV [29]. The V–SIA annihilation near tungsten GB was found to be a low energy barrier process via a replacement process along ⟨1 1 1⟩ that looked like an emitted chain of atoms towards the V [29], analogous to the visualization annihilation process near the copper GB [25]. The annihilation in tungsten bulk was also found to be a concerted process with collective and directed motion of chain of atoms. The strength of the GB sink for an SIA has been calculated to be about 2.7 eV for iron [30], which is comparable to the value of 1.6 eV obtained for copper [25] and much lower than the 7.5 eV calculated for tungsten. Considering the different sink strengths in

these systems, it may be very interesting to further explore if the proposed mechanism which has been successfully applied to copper can also be applied to iron.

In addition to the dual role of the GB as both defect sink and annihilation catalyst, several atomic mechanisms for describing the radiation resistance have also been proposed focusing on either the radiation-induced modification of the GB structure or the GB motion state, e.g., the coupled sliding-migration of GBs in tungsten under extreme stress conditions and the radiation-enhanced GB migration [16,35,36]. Here, we focus our attention on the basic interactions of radiation-induced defects with the static GB, i.e., the segregation and annihilation of SIAs and Vs near the GB. Although certain energetic and kinetic characteristics are known regarding these individual processes, they may be coupled with each other in a complicated manner, especially when considering macroscopic time scales rather than the nanosecond time scale of MD simulations. For instance, how does the SIA interact with the V prior to its segregation into the GB? In other words, does the preferential segregation of the SIA into the GB, to some extent, suppress or compete with the SIA–V recombination near the GB? After the SIA resides at the GB, does it have to reemit to recombine with the V near the GB? Or, does there exist a coupling of some sort, for instance, of the segregation/diffusion process of the SIA and the V, which promotes the SIA–V annihilation? These issues remain to be fully understood.

Considering the importance of α-iron in nuclear engineering, we selected body-centered cubic (bcc) iron as a model system in the present study. For instance, ferritic/martensitic steels with an α-iron matrix structure act as structural materials in nuclear reactors [9]. We combined MD and MS simulation with the OKMC method to investigate the radiation tolerance of nano-crystalline iron. The MD simulations of the primary radiation damage near the GBs in iron revealed fundamental processes involved in defect generation and evolution both in the grain interior and near the GB. These key processes were then parameterized utilizing MS calculations to model the diffusion and annihilation of Vs and SIAs near the GB. In this work, a modified dimer method was combined with the nudged elastic band method to investigate the annihilation mechanism in detail [37,38] because the exact mechanism for the annihilation process is still unknown. These parameterized processes were then used as a basis for the OKMC simulation to study the dynamic behavior of the diffusion and annihilation of the V and SIA near the GB on a macroscopic scale. The present work aimed to improve our knowledge of the annihilation process near the GB both at an atomistic and at a macroscopic level, in hope of understanding the role of GBs in the reduction of the radiation damage in nano-crystalline iron. Particular attention has been paid to the coupling of the basic segregation and annihilation processes near the GB.

2. Computational method

2.1. GB models and atomic potential

The GB studied in this work is a Σ5 (3 1 0)/[0 0 1] symmetric tilt GB in bcc iron, where Σ indicates the degree of geometrical coincidence at the GB, (3 1 0) denotes the plane of the GB and [0 0 1] denotes the rotation axes. The creation and relaxation procedures are identical to the procedures described in our previous work [29]. Periodic boundary conditions were applied in the two directions parallel to the GB plane, but the fixed boundary condition was selected for the direction normal to the GB plane. The simulation cells consist of a moving region sandwiched between two rigid regions, similar to simulation cells used in other studies [25,29–31]. The GB energy was minimized through the relaxation