Research Article

Capture efficiency and bias from the defect dynamics near grain boundaries in BCC Fe using mesoscale simulations

Jun Chai\textsuperscript{a,b}, Shuo Jin\textsuperscript{a,b}, Ziang Yu\textsuperscript{c,d}, Haixuan Xu\textsuperscript{c,d,e}, Guang-Hong Lu\textsuperscript{a,b,*}

\textsuperscript{a} School of Physics, Beihang University, Beijing 100191, China
\textsuperscript{b} Beijing Key Laboratory of Advanced Nuclear Materials and Physics, Beihang University, Beijing 100191, China
\textsuperscript{c} Department of Materials Science and Engineering, University of Tennessee, Knoxville, TN 37996, United States
\textsuperscript{d} Joint Institute for Advanced Materials, Knoxville, TN 37996, United States

A R T I C L E   I N F O

Article history:
Received 16 December 2020
Revised 8 February 2021
Accepted 14 February 2021
Available online 2 May 2021

Keywords:
Iron
Grain boundary
Capture efficiency
Bias
SEAKMC

A B S T R A C T

The capture efficiency describes the capability of a sink, such as a grain boundary (GB), dislocation, and void, to absorb point defects (PDs). The bias defines the difference in capture efficiency between the absorption of a vacancy and dumbbell at a sink. Complete kinetic information on PDs, including diffusion barriers and diffusion orientations, as well as accurate saddle points, are needed to determine the capture efficiency and bias at a sink accurately, which is computationally demanding. In the present study, the Self-Evolving Atomistic Kinetic Monte Carlo (SEAKMC) method was used to investigate the defect dynamics of PDs near different types of grain boundaries (GBs) (with both \{100\} and \{110\} families) accurately in body-centered cubic (BCC) iron (Fe). The capture efficiency, sink strength, and bias factor of different types of GBs were determined in Fe, which, different from traditional rate theory estimation, showed a distinct capture efficiency, sink strength, and bias in different GBs. The results demonstrate a strong positive correlation between the capture efficiency and the GB strain width, instead of the GB misorientation, GB energy, or GB-PD binding energy, which have been investigated previously. This work provides valuable insight into the radiation-induced microstructural evolution of GBs.

© 2021 Published by Elsevier Ltd on behalf of Chinese Society for Metals.

1. Introduction

Grain boundaries (GBs) play a crucial role in the metallic material properties [1–6]. GBs in irradiated materials serve as effective sinks for radiation-induced defects; hence, they influence the microstructural evolution and materials performance [5–8]. Some nanocrystalline materials, which have a high density of GBs, show improved irradiation tolerance under irradiation conditions [9,10]. This has the potential for the development of advanced structural materials highly resistant to irradiation. For example, Nita et al. showed that nanocrystalline Ni and Cu-0.5Al\textsubscript{2}O\textsubscript{3} exhibited resistance to 590 MeV proton radiation and 840 keV nickel ion irradiation damage by observing a smaller density of cracking faults tetrahedral to normal grained materials [11]. In particular, symmetric tilt GBs have been studied widely on radiation resistance in nano-GB materials through simulation, including interactions between the GB and point defects (as well as impurities, such as hydrogen and helium) or defect clusters [1,2,12–14]. Bai et al. proposed an interstitial emission mechanism through a simulation of the \Sigma11 symmetric tilt GB of Cu, leading to the annihilation of vacancies and interstitials for self-healing under irradiation [1]. Li et al., who examined several types of symmetric W GBs, reported that the GB serves as a sink for both vacancies and dumbbells and as a catalyst for vacancy-interstitial recombination by lowering the annihilation barrier, and further mitigating radiation-induced damage [13]. Jin et al. employed \Sigma5 symmetric tilt GBs to obtain an annihilation mechanism of defect clusters during irradiation, indicating a synergistic effect of GBs at a small space to significantly decrease the defect cluster density, indicating a self-healing response to radiation damage [14]. However, the current knowledge of the effects of GBs during the irradiation process is insufficient to realize the unprecedented potentials of nanocrystalline materials, which require a fundamental understanding of the correlation between the GB characteristics and the materials properties and performance.

Several experimental and theoretical techniques have been employed to study this correlation. El-Atwani et al. examined the effects of iron (Fe) GB on the irradiation tolerance experimentally from the relationship between the GB capture efficiency to irradi-
ation defects, the void-denuded zone formation, and GB geometric features [5]. Different GBs exhibited crucial distinct irradiation tolerance under similar irradiation conditions, which is complicatedly affected by the GB character, such as the GB grain size, GB misorientation, and service temperature. Ample evidence exists for a stronger capture efficiency for high angle grain boundaries (HAGB) compared to low-angle grain boundaries (LAGB) [15–17]. Moreover, several studies also declared that the Σ3 GB (which is a HAGB) has a much higher irradiation tolerance according to experimental observations [18,19]. On the other hand, some specific LAGBs show a higher or similar irradiation tolerance to some HAGBs [19]. This controversial observation suggests a complicated correlation between GB misorientations and GB irradiation tolerance. Thus, systematic studies performed under distinct conditions will be needed to generalize the correlation between the overall character of the GB capture efficiency and the performance of nanocrystalline materials.

Theoretically, the ability of a GB to absorb a specific irradiation defect can be described by its capture efficiency and sink strength [20]. Early studies modeled the GB as an ideal sphere or plane model, and the GB capture efficiency was derived with simplifications. The sink strength in the proposed formula [21] is inversely proportional to the square of the grain size, continually reflecting the information on the GB properties. Such a formula has been utilized widely to determine the sink strength [22–24]. On the other hand, the simplifications in the sink strength formula induce an identical capture efficiency to different GB types. Using a combination of accelerated molecular dynamics (AMD), adaptive kinetic Monte Carlo (AKMC) and object kinetic Monte Carlo (OKMC), Uberuaga et al. [8] reported a strong correlation between the capture efficiency and GB structure, which cannot be determined simply by the grain size. To assess the distinct GB sink efficiency, Vattré et al. [25] used an atomistic simulation to determine the sink strength determination by combining density functional theory (DFT) and OKMC in a nanoscale Cu–Ag interface. They used the developed semi- analytical method to calculate the interface stress field, and employed DFT to calculate the elastic dipole tensor for saddle point (SP) configurations for point defects (PDs) in Ag and Cu, and then calculate the capture efficiency value through an OKMC. However, the limitation of the linear elastic theory leads to a weakening exploration of the GB core effect because of the obvious configuration distortion, which has the most significant influence on the PD diffusion behavior. Another development in a capture efficiency determination is based on the standard rate theory (SRT) formula. Some groups attempted to determine the sink strength using a modified SRT formula to estimate the GB core effect. Jiang et al. [24] combined DFT and developed a SRT formula to determine the low-angle GB sink strength in Cu. Gu et al. [26] and Liu et al. [27] made similar attempts. These computational studies lacked accurate defect dynamics, which are essential for determining the capture efficiencies and sink strength. The bias represents the excessive absorption of the self-interstitial atom (SIA) over the vacancy at a sink, which can be calculated using the capture efficiency for vacancies and SIAs. A larger bias indicates more absorption of SIAs by sinks and an increasing accumulation of vacancies, which is associated closely with void swelling and the deterioration of the properties of materials.

Previous models used to calculate the capture efficiency and bias without kinetic information were the least inaccurate for the sink–PD interaction at the atomic level, particularly at the core region of the sink. Moreover, the absorption effect of vacancies was neglected, and the capture efficiency was set to 1.0 to simplify the models [10,24,28]. This causes bias associated with only the capture efficiency of SIAs. The Self-Evolving Atomistic Kinetic Monte Carlo (SEAKMC) is an atomistic on-the-fly method to acquire complete kinetic information of PD to a sink by calculating the actual SP energies [29–32]. Such a method is efficient and highly accurate for SP energy calculations. Using the kinetic information obtained from SEAKMC as inputs, a kinetic Monte Carlo (KMC) simulation with realistic diffusion paths and absorption events could be performed to determine the sink bias with much higher accuracy.

This study evaluates the capture efficiency, sink strength, and bias factors of different types of GBs in the model BCC Fe using a recently-developed method (Haixuan Xu, unpublished work) that incorporates defect dynamics to calculate the lifetime of PDs from KMC simulations. To develop a comprehensive understanding, this study considered GBs with low and high misorientation angles and a wide range of GB energies. Specifically, the migration energy barriers of PDs near different types of GBs with both (100) and (110) families in BCC Fe were calculated using the SEAKMC approach. The GB sink strength is distinct among the different GB types and is strongly affected by the GB strain distributions, grain sizes, and temperatures, which are underestimated by the SRT theory. This is the first time report of the detailed GB sink strength and bias theoretically in Fe with a completed dynamics process, which will help in the design of materials with irradiation tolerance.

2. Computational method

2.1. GB construction

Different types of symmetric tilt GBs (STGBs) in BCC Fe were constructed according to the coincidence-site lattice (CSL) theory [33,34] for the (100) and (110) families, including both low and high angle misorientations using the GB Studio software developed by Ogawa [35]. These STGBs were chosen by the GB energy results (Fig. S1), including GBs with the maximum and minimum GB energies and GBs with similar GB energies but different GB misorientations. Each STGB model contained approximately 100,000 atoms. The system was annealed using LAMMPS (Large-scale Atomic Molecular Massively Parallel Simulator) [36] with an NPT integration under three-dimensional periodic boundary conditions. Ackland et al. [37] developed the interatomic potential for the Fe–Fe system applied in this study in 2004 (A04 potential), which has been improved significantly and used widely in the last decade. After annealing, the GB energy was reduced greatly because of the significant GB structure variations. The present GB energy after annealing exhibited similar trends to those previously calculated by Tschopp et al. [17,38] and Scheiber et al. [39], from low to high misorientation angles in both the (100) and (110) family STGBs, despite the different potentials employed. The complete parameter of the selected structures and the configurations of the STGB structural units in the (100) and (110) family can be found in Table S1.

2.2. Spontaneous absorption radii

In contrast to the classic model, in which it regards the absorption radius as a planar condition with a constant both for vacancies and SIA [21,40,41], the difference in absorption events for vacancy and dumbbell were distinguished. Molecular dynamics (MD) were used to determine the spontaneous absorption radii of PDs for different constructed GBs (Fig. S2). In an NVT integration, the initial temperature was set to 300 K for the PD (dumbbell or vacancy)-containing system as an external force. The system was kept running at the same temperature for picoseconds to ensure the elapsed time was smaller than the typical diffusion time step of a PD diffusion, and then finished with a full relaxation at 0 K to determine if the dumbbell or vacancy can be absorbed by the GB. This determines the spontaneous absorption radii of the respective PDs. Vacancies and dumbbells were shown to have an entirely different absorption radius in the same GB system with different
shapes. Generally, the spontaneous absorption radii of dumbbells are two times larger than vacancies. The spontaneous absorption radii are dominated mainly by the strain field and configuration of the GB.

2.3. SEAKMC method

The SEAKMC method was introduced with an improved algorithm and efficiency to calculate the actual SP energies of PDs systematically as a function of the position at different GBs. SEAKMC is an effective method to acquire SP information at the sink region. The main features are the use of the dimer method [42] and the active volume concept [32]. The dimer method is part of a classic minimum mode SP searching method that makes the SEAKMC capable of handling a much larger system size and more complicated defects because this method reduces computational resources significantly without a direct calculation of the Hessian matrix. Using the dimer method, an initial random displacement was made for relaxation. Hence, the system is moved into an SP configuration by substantially following the minimum mode [30].

The active volume is introduced around a particular PD of interest at the sink. Only within the region of the active volume can the atoms be displaced during the SP search. In particular, all the atoms were fixed with no displacement beyond the active volume in the simulation process. The selected atoms within the active volume could move freely as a comparison, making the SP search much more effective. On the other hand, the specific active volume for different PDs will be quite different. For example, a vacancy exhibits an active volume radius of 2.7 times the lattice constant, while the dumbbell exhibits an active volume radius of 5.5 times of lattice constant in Fe.

2.4. KMC method

The SEAKMC results provide realistic diffusion paths with a diffusion direction and a barrier for the KMC simulation. In the KMC simulation, $P\alpha$ is the reciprocal of the sum of the possibility of all $N$ diffusion events introduced by Bortz et al. [43], which is given by

$$P\alpha = \frac{1}{\sum_i^n v_i^e \exp \left( \frac{-E_{a,i}}{k_b T} \right)}$$

where $v^e_i \exp \left( \frac{-E_{a,i}}{k_b T} \right)$ is the Arrhenius rate of occurrence of a diffusion event, $i$ is the identifier number of SPs, $v_i^e$ is the vibrational frequency that set to $10^{12}$ s$^{-1}$, $E_{a,i}$ is the energy barrier of event $i$, $k_b$ is the Boltzmann constant, and $T$ is the temperature in Kelvin. The energy barrier of the PDs ($E_{a,i}$) in Eq. (1) was obtained using the previous SEAKMC method.

A random number, $0 \leq \mu \leq 1$, was taken to select one diffusion event from the catalog, and the time step taken by the evolution of the selected diffusion event is given by

$$\Delta t = -\ln (\mu) \tau$$

The KMC evolution trajectories can be obtained from the initial configuration after the full energy landscape was mapped.

One PD in each atomistic coordination from the GB plane was set to the bulk area, and the lifetime was then calculated. The lifetime $t_{GB}$ for a “real walk” is defined as the elapsed time for a specific PD in completing one absorption event. The absorption event was simulated by the KMC method from the input given by the SEAKMC, including the identified diffusion barriers and directions, which provide complete diffusion paths. As a comparison, the lifetime $t_{GB}$ for a “random walk” employs the diffusion barrier value at the bulk for each position, and the diffusion paths are unified with “real walk”. One trajectory is defined as one complete diffusion event.

3. Results

3.1. Diffusion barrier and orientation

The migration energy barriers (MEBs) were determined using the SEAKMC method, which was verified by the Nudged Elastic Band (NEB) method (see Fig. 5). The $\Sigma 25/034$ GB was used as an example. Fig. 1 shows the local atomistic configuration of the GB together with the corresponding MEBs at each lattice point, which is expressed as a vector from the initial to the SP configurations. A dumbbell has six symmetrically equivalent $(110)$ orientations in BCC Fe, and each orientation possesses 12 SPs [29]. Among these, eight SPs are associated with a migration mechanism, and four SPs are related to the dumbbell rotation (Fig. S4). Fig. 1a shows the MEBs as a function of the distance to the GB. A significant variation was found when a dumbbell was close to the GB; the MEBs converge to the bulk value when the dumbbell-GB distance is large enough for both diffusion and rotation. In particular, the diffusion barrier converges to $-0.31$ eV, while the rotation barrier converges to $-0.41$ eV, which is consistent with the bulk values [44].

Diffusion vectors represent possible diffusion directions, and the magnitude corresponds to the MEB values. Fig. 1b and c present the three-dimensional and two-dimensional diffusion vector distribution, respectively, with the vectors for migration shown here only. For each specific GB system, the influence range (i.e., the distance between the GB plane and the position where MEBs coverage) for a dumbbell is greater than 30 Å. In comparison, a vacancy has eight equivalent (111) SPs. From the converged barrier distribution, the GB influence range of the $\Sigma 25/034$ GB for a vacancy was estimated to be 25 Å, which slightly smaller than that of a dumbbell. For the diffusion vector distribution, each vacancy has four pairs of SPs along the (111) direction. Each pair has the same barrier value in the bulk but different orientations (Fig. 1e). On the other hand, only four vectors are shown with the two-dimensional demonstration because the other four vectors are covered in the [100] direction (Fig. 1f). Importantly, the presence of a GB results in significant diffusion anisotropy for both the dumbbell and vacancy. Such strong anisotropy originates from the variations of the atomistic configuration and the strain field induced by the GB. The diffusion direction with the local minimum barrier dominates the most likely absorption to the GB, which is significantly anisotropic among the different GB types.

3.2. Capture efficiency

The capture efficiency is determined using the lifetime of a PD using the obtained MEBs. The KMC simulation provides the lifetime for a selected PD from a given starting position to the spontaneous absorption region with a complete diffusion process. The capture efficiency of a GB ($Z_{GB}$) is a measure of the absorption of a specific PD by the GB because of the PD-GB interaction, which can be defined as

$$Z_{GB} = \frac{J_{GB}}{F_{GB}}$$

where $J_{GB}$ and $F_{GB}$ are the diffusion flux going into the GB with the condition of a real walk and random walk, respectively, in the unit of mol/m$^2$/s. The diffusion flux $J_{GB}$ is given by

$$J_{GB} = \frac{1}{\tau_{GB}} C$$

where $C$ is the PD concentration. With the insertion of Eq. (4) into Eq. (3), the capture efficiency can be expressed as a ratio of the

---

171
lifetime (for the GB absorption time, see Fig. S6) of a “random walk” to that of a “real walk”, i.e.,

$$Z_{GB} = \frac{\tau_{GB}}{\tau_{rGB}} \quad (5)$$

With the Σ25(034) GB as an example, Fig. 2 shows the lifetime of dumbbell (Fig. 2a) and vacancy (Fig. 2b) as a function of the PD-GB distance in the case of a “real walk”. The lifetime decreased with a dumbbell or a vacancy closer to the GB, with an implication of strong GB effects on the PDs diffusion. Aided by the SEAKMC method, a clear difference in the lifetime could be observed even for the same distance to the GB. The calculated capture efficiency is shown for both the dumbbell (Fig. 2c) and vacancy (Fig. 2d) at different temperatures and grain sizes. The definition of GB grain size is the distance between two adjacent GB planes. Obviously, the capture efficiency has a strong dependence on temperature and grain size. For both a vacancy and a dumbbell, the capture effi-
ciency decreased with increasing temperature or grain size. For example, the capture efficiency of a vacancy at 300 K was 1.106 for a grain size of 20 nm, which decreased to 1.025 when the grain size was 80 nm. In the dumbbell case, at a grain size of 20 nm, the capture efficiency was 1.161 at 300 K, which decreased to 1.113 at 600 K. The capture efficiency will approach 1 when either the temperature or grain size is sufficiently high/large because $r_{GB}$ is the same as $r_{GB}$ under these conditions.

Previous studies generally employ a geometric model of GB and empirical formula to determine the capture efficiency [21,40,41]. Hence, they could not provide information on how the GB type or GB structure affects the capture efficiency of defects. For example, Tschopp et al. attempted to estimate the Fe GB capture efficiency from a view of PD formation energies. They observed a correlation between the capture efficiency and GB misorientation, including both HAGBs and LAGBs [17]. On the other hand, O. El-Atwani et al. estimated the Fe GB capture efficiency from a view of de- nuded zone formation but did not observe any dependence of the denuded zone formation on the grain size and GB misorientation for HAGBs [5]. Thus, the determination of the capture efficiency and the correlation with the GB misorientation and grain size is debated.

The absorption radius plays a crucial role in calculating the capture efficiency. The empty squares close to the GB in Fig. 1 represent the atomic positions for the absorption, the range that indicates the spontaneous absorption radii. Here, the differences in the absorption events were distinguished depending on the geometric configuration. In comparison, a GB is considered simply as an ideal planar or spherical sink in the classical SRT model. Thus, the absorption radius is typically set as a constant previously, generally a specific multiple of the lattice constant. This may lead to inaccurate and sometimes aberrant results. The distinct spontaneous absorption radii for PDs contribute to the bias calculation in a novel path, which can solve the anisotropic diffusion barrier distribution in the sink core region. The specific PD positions on the edge of the spontaneous absorption radii (the $\Sigma 41(091)$ GB was taken as an example, as shown in Fig. S3) had highly anisotropic diffusion orientations and extremely high or low diffusion barriers (also shown in Fig. S5), which strongly affect the PD absorption path over the entire system and finally influence the bias considerably. The empty squares close to the GB in Fig. 1 represent the atomic absorption positions, the range of which indicates the spontaneous absorption radii.

A strong correlation was observed between the GB spontaneous absorption radii, GB-PD binding energies distribution (for $\Sigma 41(091)$ GB see Fig. S7), and GB strain distribution. A comparison of the different planar absorption conditions with distinct constant values and spontaneous absorption radii revealed different capture efficiencies, even involving positive and negative values, as shown in Fig. S8. Obviously, dumbbells (Fig. 1c) and vacancies (Fig. 1f) have a different absorption radius in the same GB system. Generally, the spontaneous absorption radii of dumbbells are two times larger than vacancies and exhibited a different shape.

Here, the dependence of the capture efficiency (sink strength and bias) on the GB types with the input of defect dynamics was determined, as shown in Fig. 3 (and in Fig. S9). Various types of GB have different capture efficiency due to the different GB characters. At a specific temperature, the variation of the capture efficiency

Fig. 2. Lifetime and capture efficiency. The dumbbell and vacancy case in $\Sigma 25(034)$ GB is illustrated as an example. (a,b) shows the lifetime for the 10 nm grain size at 300 K by the KMC simulations. The colored points represent the distance from different PDs to the GB plane. (c,d) shows capture efficiency as a function of temperature and grain size.
for different GB types correlates with the strain field width of the GBs.

For the (100) and (110) GBs in 30 nm at 300 K, the capture efficiency of a dumbbell is larger than that of a vacancy for the same GB type. The Σ29(052) GB had the largest capture efficiency among the GB types selected, whereas the Σ5(031) GB had the lowest capture efficiency. The inset in Fig. 3 presents the strain field; the strain width was defined as the length of the strain field along the vertical direction to the GB plane, as a value over $5 \times 10^{-5}$ or less than $-5 \times 10^{-5}$. Each GB type has a unique strain width that is affected by the anisotropic configuration distribution. For all GB types selected, the capture efficiency exhibited a good positive correlation with the strain width, i.e., the GB type with a large strain width generally possesses a high capture efficiency. On the other hand, a low correlation was observed between the capture efficiency and GB misorientation angle, as shown in Fig. 3.

Considering the operating temperature in the actual nuclear reactor, detailed information of capture efficiency of dumbbells (Fig. 4a) and vacancies (Fig. 4b) were obtained as a function of the grain size at a temperature of 600 K for different types of GBs to determine the corresponding sink strength. At 600 K, different types of GBs showed a similar trend of a decrease in capture efficiency with increasing grain size, which approached 1 with a sufficiently large grain size. At a certain grain size, the capture efficiency of different types of GBs showed an obvious difference for both the dumbbell and vacancy, and such difference is enhanced with decreasing grain size. This indicates a crucial role of the GB types on the capture efficiency, which is entirely different from the approximation in previous studies.

3.3. Sink strength

We define the sink strength as

$$k^2 = \eta \frac{Z_{GB}}{L^2}.$$  

where $\eta$ is a geometric factor that depends on the simulation setup and $L$ represents the grain size. For a slab configuration, $\eta = 12$; and for a spherical GB, $\eta = 15$, which are based on previous models [21,41].

Fig. 4c and d show the sink strength of different GBs for a dumbbell and a vacancy, respectively. The sink strength decreases sharply when the grain size increases and gradually approaches zero. More importantly, the sink strength of both the dumbbell and vacancy depends on the GB types, particularly at the range of smaller grain size $\approx 10–40$ nm. Because $L^2$ is orders of magnitude larger than $Z_{GB}$, the difference in sink strength from the different GBs is not as prominent. However, the absolute value of such difference is still not negligible. For example, at a grain size of 20 nm for the dumbbell case, the maximum sink strength was 0.036 for $\Sigma 29(052)$ while the minimum was 0.032 for $\Sigma 5(031)$ with a large difference of 0.004.

Compare the present sink strength results with those from the formulations under the planar GB assumption, as shown in Fig. 4. The present sink strength is higher than the SRT ideal model but lower than Jiang’s model. Although all sink strength curves showed a similar trend and converged to zero with increasing grain size, a significant difference existed between the sink strength from the present method and the previous calculations. In the traditional SRT study, only the ‘random walk’ was counted in the sink strength.
estimation without coupling the GB effects. This makes the capture efficiency in Eq. (5) equals 1, leading to lower sink strengths. To consider the GB effects thoroughly by distinguishing a ‘random walk’ from a ‘real walk’ to obtain the correct capture efficiency (>1) in the present calculation, the sink strength, which depends on the GB types, is generally higher and becomes identical to the classical estimation from Eq. (6) at larger grain sizes, as shown in Fig. 4.

The present results were compared qualitatively with the sink strength model modified by Jiang et al. [24], despite being for low-angle GBs in face center cubic metals. (Fig. 4). To simply set the effective width as an average value of the strain region width (i.e., ~1.5 nm), the sink strength from this modified model was higher than the values obtained in the present study. This reflects the low accuracy of the previous models without considering the GB structure and detailed kinetic information, which cannot distinguish the distinct sink strength among the different GB types.

3.4. Bias factors

The bias of GB, $B_{\text{CB}}$, is defined as

$$B_{\text{CB}} = \frac{Z^v_{\text{GB}} - Z^v_{\text{GB}}}{Z^v_{\text{GB}}}$$

(7)

where $Z^v_{\text{GB}}$ and $Z^v_{\text{GB}}$ is the capture efficiency of vacancies and interstitial atoms with the presence of GBs, respectively.

Fig. 5a presents the GB bias of both the ⟨100⟩ and ⟨110⟩ family as a function of the grain size at 600 K. The differences in the bias factors of the different GBs can be seen. The figure also shows the grain size dependence of bias for one certain GB. A smaller grain size induces greater bias, and the bias decreases drastically for large grains of 120 nm. With a sufficiently large grain size, the bias approaches zero because the capture efficiencies of both the dumbbell and vacancy are equal to one. Fig. 5b presents the dramatic differences in the bias factors of GBs, which show the bias values of different GBs at 30 nm and 600 K. For the 14 types of GBs investigated in the present study, the maximum bias occurred for the Σ33[118] GB with a value of 0.058, which is more than three times higher than the minimum value, which occurs for the Σ5[031] GB with a value of 0.018.

The bias was strongly affected by the temperature. Taking the Σ25(034) GB as an example, this study illustrated how the bias varied with temperature and grain size, as shown in the inset in Fig. 5a. For example, for a smaller grain size of 20 nm, the bias at 300 K was 0.050, which decreased to 0.039 at 600 K. On the other hand, for a larger grain size of 80 nm, the bias at 300 K was 0.014, which decreases to 0.007 at 600 K. The temperature increase induced a decrease in bias simply because the capture efficiencies of the dumbbells and vacancies converge.

4. Discussion

4.1. GB character

Many experimental studies claim that the GB misorientation has a strong influence on the sink strength, suggesting that the LAGBs generally have a stronger bias than random GBs. Tschopp et al. examined the interaction between the PD and various GBs in Fe from an energy perspective [17]. LAGBs generally have a lower GB energy and lower PD-GB binding energy, suggesting better sta-
bility. However, these studies cannot explain the correlation between GB sink strength and GB misorientation thoroughly because some HAGBs (such as Σ3 and Σ5 GBs) also exhibit lower sink strengths. Tschopp also introduced another factor to examine the GB sink strength, i.e., the mean PD formation energy, which decreases with increasing GB energy. On the other hand, a low correlation was observed between the GB energies and the GB sink strength. Nevertheless, the GB excess free volume (BFV) is an essential factor in performing a GB plane mismatch, and there is a linear correlation between the GB energy and BFV [45]. The capture efficiency (also bias) showed a weak correlation with the GB energy, suggesting that the capture efficiency also has a weak correlation with the BFV of the GB.

The present work revealed a weak dependence of the GB sink strength on GB misorientation, PD formation energy, GB energy, and GB free volume. Indeed, despite the GB misorientation reflecting the complexity of a GB structure that is associated with the strain region, it was difficult to define the sink strength. Hence, a strong correlation exists between the strain width and the sink strength of the GBs (Fig. 3). The GB strain width is a dominant factor determining the sink strength, which is different from previous studies.

4.2. Correlation to experimental observations

Many groups have examined the GB performance in nanoscale irradiation tolerance materials experimentally. The relevant results revealed different sink strengths among the different GB types [5,6]. The long-term irradiation tolerance of different kinds of metals was estimated by various parameters, including PD clustering, thermal stability, and radiation-induced segregation (RIS). Although there are few direct comparisons, some correlations can still be found between the experimental observations and the present results.

The sink strength is one of the most typical parameters to measure the irradiation tolerance. The GB sink strength is often estimated experimentally through the formation of a denuded zone, which is a defect-free zone in the vicinity of the GB [19]. The denuded width was proportional to the GB sink strength, and a large experimentally observed denuded width generally corresponds to a high GB sink strength [5,19,46]. An excellent investigation by El-Atwani et al. focused on the correlation between the denuded zone and GB characteristics on Fe thin films, and the Σ3 GB was shown to have the lowest denuded zone formation energy among the GBs analyzed [5]. This agrees well with the present results that the Σ3 GB possesses a low sink strength (Figs. 3 and 4). From this view, the denuded zone barely forms near the Σ3 GB, i.e., the Σ3 GB exhibits a weak sink strength for PD absorption. On the other hand, the Σ3 GB exhibits a lower bias value (Fig. 5), indicating an inefficient effect for void swelling, which suggests that the type of Σ3 GB plays a role in enhancing the irradiation tolerance of materials. This is consistent with various experimental observations for BCC and face-centered cubic (FCC) materials [18,19,47].

5. Conclusions

This study simulated the capture efficiency and bias of (100) and (110) GBs in BCC Fe, in which the capture efficiency and bias explicitly demonstrated a strong dependence on the GB geometric structure (GB types) in addition to the grain size and temperature. With the self-developed SEAMKC method, this study could determine accurately for the first time the complete kinetic information of the diffusion barrier and orientation as well as the accurate SP distribution of different GBs in Fe. Using the complete kinetic information and spontaneous absorption radii of the respective GB as input parameters, the calculated capture efficiency, sink strength, and bias were significantly different from previous models. Different types of GBs had a distinct sink strength, and for a certain GB, the capture efficiency and sink strength decreased drastically with increasing temperature. Interestingly, the present dynamic simulation shows that the GB sink strength had a weak dependence on the GB misorientation, GB energy, PD-CB binding energy, or PD formation energy. Instead, a strong positive correlation was observed between the sink strength and the width of the GB strain region. This is the first study to determine the detailed GB capture efficiency, sink strength, and bias theoretically in Fe using a completed dynamics process, which will be quite helpful in the design of irradiation tolerance materials.

Declaration of Competing Interest

This manuscript has not been published previously and is not under consideration for publication elsewhere. The authors have no conflict of interest regarding the submission of this manuscript, and all authors approved the publication of the manuscript.
Acknowledgments

J. C., S. J., and G.-H. L. acknowledge the support by the National MCF Energy R&D Program with Grant No. 2018YFE0308103 and the National Natural Science Foundation of China with Grant No. 51871007 and 12075023. J. C. would like to thank the China Scholarship Council (CSC No. 201706021052) and University of Tennessee Knoxville (UTK) Organized Research Unit (ORU) program for supporting him a visiting student at the UTK. Z. Y. and H. X. acknowledges the support of the grant DE-SC0019151 funded by the U.S. Department of Energy, Office of Science. The authors also acknowledge the computing resources at the UTK Advanced Computing Facility.

Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.jmst.2021.02.046.

References