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Molecular Dynamics Studies of Irradiation Effects on Hydrogen Isotope Diffusion Through Nickel Crystals and Grain Boundaries

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ABSTRACT

Experiments indicated that tritium permeation in 316 austenitic stainless steel is enhanced by a factor of ~2-5 after irradiation as compared to ex-reactor results. To understand this enhancement, we have performed extensive molecular dynamics simulations to study effects of both grain boundary structure (\(\Sigma 3\{111\}, \Sigma 5\{100\} \) and \(\Sigma 11\{311\}\)) and the nature of point defects (vacancy, interstitial, and Frenkel pair) on hydrogen diffusivities in an exemplar fcc metal (nickel). By deriving diffusivities from mean square displacement, all possible atomic jump paths encountered during real diffusion are realistically sampled. By performing extremely long simulations, the statistical errors typically associated with this method are also significantly reduced. We found that within grains, interstitial defects increase diffusivity whereas vacancies have almost no effects. This mechanism might explain hydrogen permeation enhancements in
irradiated materials with coarse grains. The largest increase in hydrogen diffusivity was found at a certain combination of grain boundary and point defect. This suggests that permeability of materials with finer grains can also be enhanced by irradiation depending on whether the grain boundary character is skewed. Our results shed new light on the enhancement of tritium permeation in 316 stainless steels during reactor operations.

I. INTRODUCTION

Diffusion impacts almost all kinetic processes in solids and is therefore of broad interest. Unfortunately, diffusion parameters such as activation energy and pre-exponential factor are difficult to characterize experimentally, resulting in a large variability in reported values [1]. For example, the reported experimental activation energy barrier for hydrogen diffusion in aluminum ranges from 0.17 eV [2] to 1.45 eV [3] with the corresponding pre-exponential factor differing by 9 orders of magnitude. In this case, the measurement uncertainty may partly come from the low solubility of hydrogen in aluminum. However, significant variations in experimental values of hydrogen diffusion activation energy barrier and pre-exponential factor have also been found for the PdH$_x$ system [4] where hydrogen concentration can be as high as $x \geq 0.7$. A fundamental understanding of the diffusion is needed to elucidate experimental observations on diffusion measurements.

The effect of grain boundary structure on diffusivity is another interesting problem. For substitutional diffusion (e.g., self-diffusion), it has been long established that grain boundary diffusivity is significantly higher than that in the bulk [5]. Specifically, the grain boundary activation energy barrier is significantly lower than the bulk barrier. Although the grain boundary pre-exponential factor is also lower, the energetically activated effect can often dominate at all practical temperatures. The reduced barrier at grain boundaries can be understood because
substitutional diffusion requires open spaces for atoms to jump from one site to the other and
grain boundaries are usually associated with more and larger free volumes than the bulk. In
collection to substitutional diffusion, interstitial diffusion of small atoms does not require large
spaces. Correspondingly, effects of grain boundary structure on the diffusivities of small
interstitial atoms are more controversial. For instance, some experiments showed that hydrogen
diffusivities in single and polycrystalline nickel are similar [6,7,8,9], whereas others indicated that
they are different [6,10,11,12,13]. Despite extensive studies in the past, many questions remain
unanswered. For example, how does the in-plane (within the grain boundary) diffusivities differ
from the out-plane (away from the grain boundary) diffusivities? What are the effects of grain
boundary network (specifically, junction regions of neighbouring grains)? Fundamental studies
are required to better understand grain boundary diffusion.

Hydrogen diffusion in metals is also a hot topic. First, hydrogen diffusion impacts the
hydrogen embrittlement [14], which is a major material problem inhibiting the wide application
of hydrogen energy [15]. The diffusion of hydrogen isotopes under irradiation conditions also
presents major technological issues for nuclear energy applications. For example, experiments
indicated that tritium permeation in austenitic stainless steel is subsequently enhanced after
irradiation as compared to ex-reactor results [16,17,18,19,20]. Understanding mechanisms of this
enhancement is critical to develop improved materials for reactor operations.

To better understand how hydrogen migration is affected by other defects in face-centred-
cubic (fcc) materials such as austenitic alloys, the present work performs extensive molecular
dynamics (MD) simulations of hydrogen diffusion in an exemplar fcc metal nickel. Bulk diffusion
in single crystals, the in-plane and out-plane diffusion for three representative low-Σ grain
boundaries (Σ3{111}, Σ5{100}, and Σ11{311}), crystals free of point defects and containing
three types of point defects (vacancy, interstitial, and Frenkel pair), are all studied. It should be noted that for systems containing grain boundaries and point defects, hydrogen atoms may encounter enormous distinct atomic jump paths not known \textit{a priori}. As a result, the nudged elastic band method for individually calculating the energy barrier of predesignated atomic jump path \[21,22,23\] is not applicable. Instead, we perform MD simulations to calculate mean square displacement (MSD) of hydrogen atoms, deriving diffusivities from the MSD, and computing the overall diffusion energy barrier by fitting the diffusivities obtained at different temperatures to Arrhenius equation. Note that this approach is not widely applied in literature due to its large statistical error. This is not an issue in the present work as the computational resources that we can access allow us to perform extensive, extremely long MD simulations to significantly reduce the statistical error.

II. METHODS

A. \textit{Interatomic Potential}

We used the Ni-H embedded atom method potential developed by Angelo \textit{et al.} [24]. This potential has been fitted to the experimental lattice constant, cohesive energy, elastic constants, vacancy formation energy, stacking fault energy, and surface energy of nickel, and matches well experimental values of heat of solution, molar volume, and bulk diffusion energy barrier of hydrogen.

B. \textit{Molecular Dynamics Methods}

We considered three bi-crystals containing respectively the $\Sigma 3\{111\}$, $\Sigma 5\{100\}$, and $\Sigma 11\{311\}$ grain boundaries, as well as a single crystal ($\Sigma 1$) without any grain boundary. As shown in Fig. 1, the grain boundary planes for all bi-crystals are parallel to the x-z plane, with crystals below and above the boundary having the same size. The size and geometry of the
computational cells are summarized in Table I. Note that once the grain boundary type and the crystal below the grain boundary are given, the crystal above the grain boundaries is uniquely determined. Hence, we only list the information of the lower grain in Table I. Periodic boundary conditions are used in all the three coordinate directions.

**Fig. 1. Schematic of model bi-crystals.**

**Table I.** Number and type of atomic planes in the three coordinate directions, and number of atoms in the computational cell. For the bi-crystal systems, only information of the lower grain is provided.

<table>
<thead>
<tr>
<th>Single Crystal</th>
<th>Σ3{111}</th>
<th>Σ5{100}</th>
<th>Σ11{311}</th>
</tr>
</thead>
<tbody>
<tr>
<td>plane # and type</td>
<td>atom #</td>
<td>plane # and type</td>
<td>atom #</td>
</tr>
<tr>
<td>x</td>
<td>y</td>
<td>z</td>
<td>x</td>
</tr>
<tr>
<td>15 (112)</td>
<td>12 (111)</td>
<td>8 (110)</td>
<td>960</td>
</tr>
<tr>
<td>10 (100)</td>
<td>3 (010)</td>
<td>10 (001)</td>
<td>1200</td>
</tr>
</tbody>
</table>

We also considered the effects of three point defects: vacancy, interstitial, and Frenkel (vacancy-interstitial) pair. These defects were studied separately. Using the nickel crystals created as described above, the relevant numbers of hydrogen and defects were introduced uniformly into
the system. Here the hydrogen and defect concentrations were fixed at 2% and 0.5% respectively. These concentrations are higher than those commonly measured in experiments. However, previous studies [1,4] indicate that at these concentrations, hydrogen and defects still behave individually as in a dilute solution.

C. Derivation of Diffusion Parameters

The same MD diffusion simulation method developed previously [1] was used. Briefly, an MD simulation is performed for a total time $t_{MD}$. Let the positions of hydrogen atoms be notated as $\alpha_i$, where $\alpha = x, y, z$ represents coordinates and $i = 1, 2, \ldots, N$ represents all the hydrogen atoms in the system. The time dependence of these coordinates, $\alpha_i(t)$ are recorded on a time interval of $\Delta t$, i.e., at times of $t = j\Delta t, j = 1, 2, \ldots, m \ (m = t_{MD}/\Delta t)$, where $\Delta t$ can be any multiple of the time step size $dt$ used in the MD simulations. These recorded coordinates can be used to calculate hydrogen diffusion displacement at discrete diffusion times. For instance, the displacement of a hydrogen atom $i$ over a $k\Delta t$ period can be calculated as $\Delta \alpha_{i,j}(k\Delta t) = \alpha_i(j\Delta t-\Delta t+k\Delta t) - \alpha_i(j\Delta t-\Delta t)$ if we assume that the starting and ending times of this displacement are $j\Delta t-\Delta t$ and $j\Delta t-\Delta t+k\Delta t$ respectively. Clearly, for a given $k\Delta t$, $j$ can vary from 1 to $m+1-k$, resulting in multiple measurements of the displacement. The number of such measurements is large when $m$ is large and $k \ll m$. Under such conditions, we can calculate highly converged mean square displacement of all hydrogen atoms from:

$$\left\langle \left[ \Delta \alpha(k\Delta t) \right]^2 \right\rangle = \frac{\sum_{j=1}^{m+1-k} \sum_{j=1}^{m} \left[ \Delta \alpha_{i,j}(k\Delta t) \right]^2}{N(m+1-k)}$$

(1)

The mean square displacement is a linear function of time $t$. Specifically, if $D_\alpha$ represents diffusivity along the $\alpha$ ($\alpha = x, y, z$) direction, $D_{xz}$ represents diffusivity on the xz plane, and $D_{xyz}$ represents the bulk diffusion, we have
\[
\begin{align*}
\langle \Delta x(k\Delta t)^2 \rangle &= 2D_x t \\
\langle \Delta y(k\Delta t)^2 \rangle + \langle \Delta z(k\Delta t)^2 \rangle &= 4D_{yz} t \\
\langle \Delta x(k\Delta t)^2 \rangle + \langle \Delta y(k\Delta t)^2 \rangle + \langle \Delta z(k\Delta t)^2 \rangle &= 6D_{xyz} t
\end{align*}
\]

(2)

Fitting the MD mean square displacement data to Eq. (2) in a small-time range \( t_f << t_{MD} \) (i.e., \( k = t_f/\Delta t << m = t_{MD}/\Delta t \)) allows us to determine highly converged diffusivities. This procedure can be used to calculate diffusivities at different temperatures. The results can then be fitted to the Arrhenius equation to get the activation energy \( Q \), and the pre-exponential factor \( D_0 \).

In this work, we performed MD diffusion simulations at 13 temperatures \( T = 300, 325, 350, \ldots, 600 \) K by increments of 25K to construct an Arrhenius relation for each of the 16 cases (4 different crystal systems each with and without the 3 different point defects). This leads to a total of 208 simulations. To produce highly converged results, all our simulations ran for an extremely long time of \( t_{MD} = 4.4 \times 10^2 \) ns, with other model parameters fixed at \( dt = 5.0 \times 10^{-7} \) ns, \( \Delta t = 1.1 \times 10^{-2} \) ns, and \( t_f = 18 \) ns. Molecular dynamics code LAMMPS [25,26] was used for all simulations at temperature and pressure damping coefficients of 0.05 and 0.5 ps respectively.

**III. RESULTS**

For clarity, the activation energies \( Q \) and pre-exponential factors \( D_0 \) derived by fitting our MD simulations are first summarized in Table II for all the cases whereas their discussion will be provided at relevant places below. Note that for single crystals where hydrogen diffusion properties are isotropic, we found very closely that \( Q_x = Q_y = Q_z = Q_{xy} = Q_{xz} = Q_{yz} = Q_{xyz} \), and \( D_{0,x} = D_{0,y} = D_{0,z} = D_{0,xy} = D_{0,xz} = D_{0,yz} = D_{0,xyz} \). As a result, we only show the three dimensional isotropic values of \( Q_{xyz} \) and \( D_{0,xyz} \) because they are averaged over the biggest data set and hence are associated with the lowest statistical errors. Likewise, for systems containing an isotropic grain boundary, we only show the in-plane properties \( Q_{xz} \) and \( D_{0,xz} \), along with the out-plane...
properties \( Q_y \) and \( D_{0,y} \). If the grain boundary is anisotropic, we further split the in-plane properties to \( Q_x, Q_z \) and \( D_{0,x}, D_{0,z} \). Note also that for \( \Sigma 3\{111\} \) grain boundary with interstitial, two sets of results are provided. This is because we found two interfacial reconstructions caused by the interstitial, and the two sets of results correspond to the two reconstructions to be discussed below.

Table II. Activation energies \( Q \) and pre-exponential factors \( D_0 \) for different cases. Note that subscript “xyz” indicates isotropic bulk diffusion, “y” indicates out-plane diffusion, “xz” indicate isotropic in-plane diffusion, “x” and “z” indicate that the anisotropic in-plane diffusion is further split into two directions.

<table>
<thead>
<tr>
<th></th>
<th>No defects</th>
<th>Vacancies</th>
<th>Interstitials</th>
<th>Frenkel pairs</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Single crystals</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( Q_{xyz} ) (eV)</td>
<td>0.508</td>
<td>0.455</td>
<td>0.407</td>
<td>0.435</td>
</tr>
<tr>
<td>( D_{0,xyz} ) (Å²/ps)</td>
<td>3.835×10^2</td>
<td>8.925×10^1</td>
<td>5.959×10^1</td>
<td>9.075×10^1</td>
</tr>
<tr>
<td><strong>( \Sigma 3{111} )</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( Q_x ) (eV)</td>
<td>0.483</td>
<td>0.465</td>
<td>0.441</td>
<td>0.302</td>
</tr>
<tr>
<td>( D_{0,x} ) (Å²/ps)</td>
<td>2.283×10^2</td>
<td>1.190×10^2</td>
<td>2.336×10^2</td>
<td>1.553×10^1</td>
</tr>
<tr>
<td>( Q_z ) (eV)</td>
<td>0.475</td>
<td>0.448</td>
<td>0.453</td>
<td>0.453</td>
</tr>
<tr>
<td>( D_{0,z} ) (Å²/ps)</td>
<td>1.666×10^2</td>
<td>8.089×10^1</td>
<td>1.547×10^2</td>
<td>1.503×10^4</td>
</tr>
<tr>
<td><strong>( \Sigma 5{100} )</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( Q_x ) (eV)</td>
<td>0.395</td>
<td>0.301</td>
<td>0.291</td>
<td>0.300</td>
</tr>
<tr>
<td>( D_{0,x} ) (Å²/ps)</td>
<td>8.623×10^1</td>
<td>3.376×10^1</td>
<td>1.413×10^4</td>
<td>2.073×10^1</td>
</tr>
<tr>
<td>( Q_z ) (eV)</td>
<td>0.716</td>
<td>0.672</td>
<td>0.864</td>
<td>0.747</td>
</tr>
<tr>
<td>( D_{0,z} ) (Å²/ps)</td>
<td>2.289×10^1</td>
<td>1.116×10^2</td>
<td>1.767×10^9</td>
<td>5.497×10^1</td>
</tr>
<tr>
<td><strong>( \Sigma 11{311} )</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( Q_x ) (eV)</td>
<td>0.476</td>
<td>0.395</td>
<td>0.393</td>
<td>0.391</td>
</tr>
<tr>
<td>( D_{0,x} ) (Å²/ps)</td>
<td>1.271×10^2</td>
<td>2.907×10^1</td>
<td>4.808×10^1</td>
<td>2.888×10^1</td>
</tr>
<tr>
<td>( Q_z ) (eV)</td>
<td>0.493</td>
<td>0.447</td>
<td>0.432</td>
<td>0.465</td>
</tr>
<tr>
<td>( D_{0,z} ) (Å²/ps)</td>
<td>3.474×10^4</td>
<td>1.262×10^4</td>
<td>1.983×10^2</td>
<td>2.420×10^4</td>
</tr>
<tr>
<td>( Q_y ) (eV)</td>
<td>0.655</td>
<td>0.703</td>
<td>0.627</td>
<td>0.620</td>
</tr>
<tr>
<td>( D_{0,y} ) (Å²/ps)</td>
<td>1.388×10^4</td>
<td>3.342×10^2</td>
<td>1.528×10^2</td>
<td>8.077×10^4</td>
</tr>
</tbody>
</table>

A. **Single Crystal Diffusivities**

To provide a benchmark reference for revealing grain boundary effects, MD diffusivities results obtained for the single crystals are summarized in Fig. 2, where the lines are calculated from the Arrhenius based on the parameters shown in Table II. Multiple interesting phenomena
can be found from Fig. 2. First, all MD data points fall closely on the linear Arrhenius plots, confirming the high convergence of the simulations. With the convergence established, we can confidently conclude that vacancies do not significantly change diffusion as the data points obtained from systems with and without vacancies are essentially indistinguishable within the error of the method. On the other hand, interstitials most significantly promote diffusion. Specifically, the MD data points shown in Fig. 2 indicate that diffusivities for systems containing interstitials are about 16.3 times at 300 K and about 1.4 times at 600 K as compared to diffusivities without any defects. The increased diffusivities are reflected not only by their highest values, but also by their smallest absolute value of slope (see also the activation energy in Table II). Frenkel pairs have an intermediate effect between interstitials and vacancies, despite that the total number of point defects (interstitials + vacancies) is doubled. This can be easily understood because some interstitials and vacancies can annihilate, resulting in a decrease of the effective interstitial or vacancy density.

![Fig. 2](image)

**Fig. 2.** Effects of various point defects on Arrhenius behaviour of xyz diffusion of hydrogen in single crystalline nickel. Lines are calculated based on parameters shown in Table II.

The higher hydrogen diffusivity enhancement by interstitial than by vacancy can also be understood. First, the binding energy between hydrogen and interstitial is lower than that between...
hydrogen and vacancy as will be show below. Thus, vacancy is more effective to trap hydrogen.

Second, vacancy diffusion energy barrier is usually much higher than interstitial diffusion energy barrier in metals [27]. Thus, hydrogen-vacancy complex is less mobile than hydrogen-interstitial complex. Our system contains many diffusion paths so that the effects of interstitials and vacancies are more complex. We will further examine this below.

B. $\Sigma3\{111\}$ Grain Boundary

(1) Diffusivities

The in-plane and out-plane diffusivities obtained from the MD simulations for the $\Sigma3\{111\}$ grain boundary cases are summarized in Figs. 3(a) and 3(b) respectively. To clearly show the grain boundary effects, the fitted single crystalline, defect-free data as shown by the black line in Fig. 2 is reproduced in Figs. 3(a) and 3(b) as the thick light-grey lines. Again, MD data points are seen to generally fall on the linear Arrhenius plots, confirming the convergence of the simulations.

![Fig. 3](image)

**Fig. 3.** Effects of various point defects on Arrhenius behaviour of (a) xz, and (b) y diffusion of hydrogen in a nickel crystal containing a $\Sigma3\{111\}$ grain boundary on the xz plane. Lines are calculated based on parameters shown in Table II.
Additional important phenomena can be found in Fig. 3. First, in the absence of point defects, not only the in-plane and out-plane diffusivities are same, but they are pretty much close to the bulk diffusivity for a single crystal. Because the coherent twin boundary ($\Sigma 3\{111\}$) does not have any impact on hydrogen diffusion, it does not trap hydrogen. Like the single crystal case, vacancies do not change the in-plane and out-plane diffusivities at least within the error margin. However, interstitials noticeably increase the in-plane diffusivity and slightly increase the out-plane diffusivities. Specifically, the MD data points shown in Fig. 3(a) indicate that the in-plane diffusivities with interstitials are about 15.3 times at 300 K and about 2.3 times at 600 K as compared to the in-plane diffusivities without any point defects. The reason that interstitial more effectively increases hydrogen diffusivity than vacancy has been discussed above. This observed interstitial effect is reflected in Table II where the in-plane diffusion barrier with interstitials is the smallest. Note that in Table II, there are two sets of data listed for interstitials. The set derived from Fig. 3 is listed at the left column and the right column is obtained from additional simulations to be discussed below. Finally, Fig. 3 indicates that Frenkel pairs also increase the in-plane and out-plane diffusivities, but not as significantly as interstitials. Again, this can be understood because some interstitials and vacancies annihilate resulting in a reduced interstitial density.

(2) Grain Boundary Structure Visualization

To understand the effects of interstitials and vacancies on the $\Sigma 3\{111\}$ grain boundary, the atomic configurations of the grain boundary without defects, with interstitials, and with vacancies are examined respectively in Figs. 4(a) – 4(b), where Ni atoms in the upper and lower grains are shown as big balls in dark and light grey scales respectively, and H atoms are shown as small balls in blue. Here all configurations are obtained after 111 ns MD simulation at 600 K. To show
the population of interstitials and vacancies, number of Ni atoms in each atomic layer is indicated in Figs. 4(b) and 4(c).

![Diagram showing configurations of a Σ3{111} grain boundary with defects](image)

**Fig. 4.** Effects of various point defects on the configurations of a Σ3{111} grain boundary: (a) no point defects, (b) interstitials, and (c) vacancies.

Many interesting results can be obtained from Fig. 4. First, no clear hydrogen segregation to the grain boundary can be observed in Fig. 4, confirming the conclusion obtained above that the Σ3{111} grain boundary does not trap hydrogen. Second, there are extra Ni interstitials at the bottom and extra Ni vacancies near the top. Note that under the periodic boundary conditions, bottom and top are both at the same grain boundary. In addition, the bottom (or top) grain boundary is structurally equivalent to the middle grain boundary and the segregation to the bottom (or top) grain boundary but not to the middle grain boundary is purely statistical. Hence, Fig. 4 indicates that the Σ3{111} grain boundary traps nickel interstitials and vacancies. Third, segregation of interstitials to the grain boundary changes the orientation of the atomic rows. For instance, as indicated by the red arrows in Figs. 4(a), the atomic rows from back atoms to front atoms point to the left in the system free of any point defects. However, the bottom red arrow in Fig. 4(b) indicate that on the plane containing most Ni interstitials, the atomic rows from back atoms to front atoms point to the right. This rotation of atomic rows can be viewed as a
mechanism to relax stresses. Fourth, the red circles in Figs. 4(b) and 4(c) indicate some light Ni atoms in the dark Ni layer or vice versa, meaning that substitutional diffusion of Ni atoms occurred when either interstitials or vacancies are present. As expected, such a substitutional diffusion did not occur in the absence of interstitials and vacancies as shown in Fig. 4(a). Finally, we point out that the interatomic potential we used cannot simulate the formation of H₂ molecules, and the observation of some pairs of atoms in Fig. 4 is an artefact of the 2D projection.

To further explore the statistical nature of the grain boundary structures, we examine two additional atomic configurations of the Σ3{111} grain boundary with interstitials. These two configurations are obtained from 111 ns MD simulations at 300 K and 500 K, and are shown respectively in Figs. 5(a) and 5(b) using the same scheme as Fig. 4. The configuration shown in Fig. 5(b) is statistically close to the one shown in Fig. 4(b). Specifically, all the five Ni interstitials segregate to the bottom grain boundary, which causes the atomic rows on the grain boundary plane to change the orientation. In contrast, the configuration shown in Fig. 5(a) is different. Here, three of the five interstitials segregate to the bottom boundary and the other two interstitials segregate to the middle boundary. Because interstitial density on each of the grain boundaries is reduced, rotation of atomic rows does not occur except that some atomic rows on the middle grain boundary becomes less well defined. As stated above, there are no thermodynamic reasons of preferential occupation of interstitial atoms on either grain boundary, and the difference between Figs. 5(a) and 5(b) is primarily statistical. For convenience, we refer to the 300 K configuration shown in Fig. 5(a) as Σ3a{111}, and the 500 K configuration shown in Fig. 5(b) as Σ3b{111}. An interesting question then arises: will the two different configurations shown in Figs. 5(a) and 5(b) have different hydrogen diffusivities. This question will be answered in the next section.
Fig. 5. Two different $\Sigma 3\{111\}$ grain boundary configurations at the presence of Ni interstitials obtained from 111 ns MD simulations at (a) 300 K, and (b) 500 K.

(3) Effects of Statistical Configurations on Diffusivities with Interstitials

The diffusivities shown in Fig. 3 are based on simulations where the initial grain boundary was manually created without any reconstruction. Fig. 5 indicates that at a given bulk density of nickel interstitials, the $\Sigma 3\{111\}$ grain boundary can reconstruct into two different configurations depending on a statistical accumulation of nickel interstitials at the grain boundary. Hence, we re-calculate diffusivities with the initial grain boundary taken as either the 300 K configuration shown in Fig. 5(a) or the 500 K configuration shown in Fig. 5(b). The results of diffusivities are summarized in Fig. 6(a) for the in-plane diffusion and Fig. 6(b) for the out-plane diffusion, where again the defect-free bulk diffusivities are shown as the thick grey lines for benchmark comparison.
Fig. 6. Effects of initial configuration on Arrhenius behaviour of (a) xz, and (b) y diffusion of hydrogen in Ni crystals containing Ni interstitials and a $\Sigma3\{111\}$ grain boundary on the xz plane. Lines are calculated based on parameters shown in Table II.

Multiple interesting results can be found in Fig. 6. First, the diffusivities obtained from the 300 K initial configuration are very close to those shown in Fig. 3, indicating that these results are relatively reproducible provided that the density of nickel interstitials at the grain boundary is given. On the other hand, if the irradiation causes nickel interstitials to concentrate on one $\Sigma3\{111\}$ grain boundary so that the interstitial density at the boundary is high enough to cause the boundary to reconstruct into the 500 K configuration shown in Fig. 5(b), then the in-plane diffusivities are significantly increased. Specifically, the MD data points shown in Fig. 6(a) indicate that the in-plane diffusivities with the 500 K reconstructed grain boundary are about 146.7 times at 300 K and about 2.4 times at 600 K as compared to the in-plane diffusivities without any point defects. This increase is associated with a significant decrease in the absolute value of slope and hence the energy barrier as can be seen in Table II. This point illustrates the role of the grain boundary structure on the diffusivities. Finally, the initial configurations do not have any effects on the out-plane diffusivities. This can be understood because the reconstruction occurs mainly on the grain boundary plane so that it does not impact the diffusion in the direction normal to the boundary.
We also performed the same additional simulations (i.e., taking the final configurations obtained at different temperatures in the first set of simulations as the starting samples to perform the second set of simulations) for other defects and other grain boundaries. No changes of diffusivities were observed.

C. Σ5{100} Grain Boundary

(1) Diffusivities

The in-plane and out-plane diffusivities obtained from the MD simulations for the Σ5{100} grain boundary cases are summarized in Figs. 7(a) and 7(b) respectively. Again, the fitted single crystalline, defect-free data as shown by the black line in Fig. 2 is reproduced in Figs. 7(a) and 7(b) as the thick light-grey lines. Here, MD data points are seen to generally fall on the linear Arrhenius plots in Fig. 7(a), confirming the convergence of the simulations on the in-plane diffusion. The MD data points shown in Fig. 7(b) can be divided into two linear regimes corresponding to separate Arrhenius behaviours at high and low temperatures.

Fig. 7. Effects of various point defects on Arrhenius behaviour of (a) xz and (b) y diffusion of hydrogen in a nickel crystal containing a Σ5{100} grain boundary on the xz plane. Lines are calculated based on parameters shown in Table II.
Additional important phenomena can be found in Fig. 7. First, it can be seen from Fig. 7(a) that the point defects significantly increase the in-plane diffusivity of hydrogen on the $\Sigma 5\{100\}$ gain boundary. Interestingly, diffusivities with interstitials are no longer the highest. Instead, diffusivities with presence of vacancies are the highest. Specifically, the MD data points shown in Fig. 7(a) indicate that the in-plane diffusivities with vacancies are about 9.2 times at 300 K and about 2.2 times at 600 K as compared to the in-plane diffusivities without any point defects. Related to the increases in diffusivities, Table II indicates that all point defects reduce the activation energies of the in-plane diffusion. On the other hand, Fig. 7(b) shows that the out-plane diffusivities are significantly lower than the bulk diffusivities, suggesting that hydrogen atoms are trapped by the $\Sigma 5\{100\}$ gain boundary. The trapping effect is further confirmed by the two segments of the Arrhenius plots. In the low temperature range, diffusivities are extremely low and are nearly independent of temperature. This means that hydrogen atoms no longer diffused out of the grain boundary once they reached there. In the high temperature range, hydrogen atoms could overcome the trap and continuously diffused out of the grain boundary. As expected, this is associated with much larger activation energy barriers as reflected by the slopes in the high temperature regimes in Fig. 7(b). Because diffusion only occurs when hydrogen atoms overcome the trap, the energy barriers listed in Table II are fitted to the high temperature data. The thin solid lines shown in Fig. 7(b) are based on such fits.

Unlike the bulk and $\Sigma 3\{111\}$ in-plane diffusion, vacancy increases hydrogen diffusivity on the $\Sigma 5\{100\}$ grain boundary more than interstitial. This is because the initial and final sites of a jumping hydrogen atom can no longer be clearly defined as octahedral and tetrahedral sites on the $\Sigma 5\{100\}$ grain boundary. This will be further analysed in detail below.

(2) Grain Boundary Structure Visualization
To understand the effects of interstitials and vacancies on the $\Sigma 5\{100\}$ grain boundary, configurations obtained after 111 ns MD simulation at 550 K are analysed. Specifically, the atomic configurations of the grain boundary without point defects, with interstitials, and with vacancies are examined respectively in Figs. 8(a) – 8(c). Again, Ni atoms in the upper and lower grains are shown as big dark and light balls, H atoms are shown as small blue balls, and number of Ni atoms in each atomic layer is indicated in Figs. 8(b) and 8(c).

![Diagram showing configurations of grain boundary with and without point defects](image)

Fig. 8. Effects of various point defects on configurations of a $\Sigma 5\{100\}$ grain boundary: (a) no point defects, (b) interstitials, and (c) vacancies.
Many interesting results can be obtained from Fig. 8. First, almost all hydrogen atoms are seen at the grain boundary, confirming the conclusion obtained above that the $\Sigma 5\{100\}$ grain boundary traps hydrogen. Second, it can be seen from Figs. 8(b) and 8(c) that all Ni interstitials and Ni vacancies are populated near either the bottom/top or middle grain boundaries, indicating that the $\Sigma 5\{100\}$ grain boundary also traps Ni interstitials and Ni vacancies. Third, segregation of interstitials or vacancies at the grain boundary does not change the orientation of the atomic rows. For instance, Fig. 8(a) indicates that in the system free of interstitials and vacancies, the atomic rows in the upper (dark) layer always point to the right, and the atomic rows in the lower (light) layer always point to the left. Such orientations of atomic rows are retained in Figs. 8(b) and 8(c) despite the presence of interstitials and vacancies. Note that the interstitial density is high near the top/bottom boundary where almost all nickel interstitials are populated. Finally, the red circles in Figs. 8(b) and 8(c) confirm the expected result that substitutional diffusion of Ni atoms occurred when either interstitials or vacancies were present.

As stated above, we also performed additional simulations to compute diffusivities using different initial configurations. No significant changes of diffusivities were found.

D. $\Sigma 11\{311\}$ Grain Boundary

(1) Diffusivities

The structure of the $\Sigma 11\{311\}$ grain boundary is geometrically anisotropic, so it is possible that its in-plane diffusivities are different in x and z directions. As a result, we calculate diffusivities in the x, z, and y directions separately. The diffusivity results are summarized in Figs. 9(a) and 9(b) for the in-plane x and z directions respectively, and in Fig. 9(c) for the out-plane direction y. Again, the fitted single crystalline, defect-free data as shown by the black line in Fig. 2 is reproduced in Figs. 9(a) - 9(c) as the thick light-grey lines. Like Fig. 7(a), the MD data points
are seen to generally fall on the linear Arrhenius plots in Figs. 9(a) and 9(b), confirming the convergence of the simulations on the in-plane diffusion. Like Fig. 7(b), the MD data points shown in Fig. 9(c) can be divided into two linear regimes corresponding to separate Arrhenius behaviours at high and low temperatures.

Additional important phenomena can be found in Fig. 9. First, it can be seen from Figs. 9(a) and 9(b) that the point defects significantly increase the in-plane diffusivity of hydrogen on the Σ11{311} grain boundary, especially for interstitials. Specifically, the MD data points shown in Fig. 9(a) indicate that the in-plane diffusivities along the x [\(0\overline{1}1\)] direction with interstitials are about 5.9 times at 300 K and about 1.9 times at 600 K as compared to the same in-plane diffusivities without any point defects. Similarly, the MD data points shown in Fig. 9(b) indicate that the in-plane diffusivities along the z [\(\overline{2}33\)] direction with interstitials are about 4.1 times at 300 K and about 1.9 times at 600 K as compared to the same in-plane diffusivities without any point defects. Our results also suggest the existence of some differences of diffusion in the x and z directions, as such difference cannot be attributed to statistical errors due to the high convergence of simulations. Such conclusion is strong since we have decomposed the single crystal xyz diffusivities shown in Fig. 2 in the x, y, and z directions, and the in-plane xz diffusivities of the Σ3{111} and Σ5{100} grain boundaries in the x and z directions. We found that in these isotropic cases, the decomposed diffusivities are all aligned on top of each other with the undecomposed values, with the fitted activation energy barriers matching to the 2\(^{nd}\) and in most cases the 3\(^{rd}\) decimal point. Comparison between Figs. 9(a) and 9(b) indicates that the differences in the x and z diffusivities are even larger when the interstitials are replaced by the vacancies or Frenkel pairs.
Fig. 9. Effects of various point defects on Arrhenius behaviour of (a) x, (b) z, and (c) y diffusion of hydrogen in a nickel crystal containing a $\Sigma 11\{311\}$ grain boundary on the xz plane. Lines are calculated based on parameters shown in Table II.
The finding of the increases of diffusivities due to defects are consistent with Table II where all point defects reduce the activation energies of the in-plane diffusion. On the other hand, Fig. 9(c) shows that the out-plane diffusivities are significantly lower than the bulk diffusivities, suggesting that hydrogen atoms are trapped by the $\Sigma 11\{311\}$ gain boundary. Like Fig. 7, the trapping effect is further confirmed by the two segments of the Arrhenius plots. The plots in the high temperature range measure the de-trapping energy barrier. Because diffusion only occurs when hydrogen atoms overcome the trap, the energy barriers listed in Table II are fitted to the high temperature data. The lines shown in Fig. 9(c) are based on such fits.

(2) Grain Boundary Structure Visualization

To understand the effects of interstitials and vacancies on the $\Sigma 11\{311\}$ grain boundary, configurations obtained after 111 ns MD simulation at 600 K are analysed. Specifically, the x-y projection (front view) of the atomic configurations of the grain boundary without point defects, with interstitials, and with vacancies are examined separately in Figs. 10(a) – 10(c), and an example of the y-z projection (side view) of the configuration is shown in Fig. 10(d). Again, Ni atoms in the upper and lower grains are shown as big dark and light balls, H atoms are shown as small blue balls, and number of Ni atoms in each atomic layer is indicated in Figs. 10(b) and 10(c).

Many interesting results can be obtained from Fig. 10. First, almost all hydrogen atoms are seen near the grain boundary, confirming the conclusion obtained above that the $\Sigma 11\{311\}$ grain boundary traps hydrogen. Second, it can be seen from Figs. 10(b) and 10(c) that all Ni interstitials and Ni vacancies are populated near either the bottom/top or middle grain boundaries, indicating that the $\Sigma 11\{311\}$ grain boundary also traps Ni interstitials and Ni vacancies. Third, segregation of interstitials or vacancies at the grain boundary does not change the orientation of the atomic
rows that are perpendicular to the image plane in Figs. 10(a) – 10(c). Finally, the red circles in Figs. 10(b) and 10(c) confirm the expected result that substitutional diffusion of Ni atoms occurred when either interstitials or vacancies were present.

Fig. 10. Effects of various point defects on configurations of \( \Sigma 11\{311\} \) grain boundary. (a) no point defects, (b) interstitials, (c) vacancies, and (d) an illustration of side projection.

As stated above, we also performed additional simulations to compute diffusivities using different initial configurations. No significant changes of diffusivities were found.

**IV. ENERGETICS STUDIES**

To understand the hydrogen population, MD simulations were performed at 100 K for 1.1 ns for various systems where a hydrogen atom is placed in bulk, near various grain boundaries, far away from various point defects, and near various point defects. After discarding the first 0.1 ns,
highly converged time-averaged total system energies were obtained from the remaining 1.0 ns simulations. We verified that the 100 K temperature did not cause a migration of the hydrogen atom from its initial location and the finite temperature MD simulations better relaxed the systems than the 0 K molecular statics (MS) simulations. From these energies, hydrogen interaction energy with various grain boundaries and point defects were obtained, and the results are summarized in Table III. Table III indicates that hydrogen atoms are attracted to both nickel interstitials and nickel vacancies, suggesting that even a very low concentration of point defects can impact hydrogen diffusion. Table III also indicates that hydrogen atoms are attracted to all the three grain boundaries, but the attractive energy on the $\Sigma 3\{111\}$ is negligibly small compared to those on $\Sigma 5\{100\}$ and $\Sigma 11\{311\}$. This suggests that $\Sigma 5\{100\}$ and $\Sigma 11\{311\}$ grain boundaries have significant hydrogen trapping effects whereas $\Sigma 3\{111\}$ has negligible effects. All these corroborate well the MD results discussed above.

Table III. Interaction energies (eV) between hydrogen and various point defects and grain boundaries

<table>
<thead>
<tr>
<th>Point defects</th>
<th>Grain boundaries</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vacancies</td>
<td>$\Sigma 3{111}$</td>
</tr>
<tr>
<td>-0.18</td>
<td>-0.03</td>
</tr>
<tr>
<td>Interstitials</td>
<td></td>
</tr>
<tr>
<td>-0.12</td>
<td></td>
</tr>
</tbody>
</table>

To achieve an energetics understanding on how grain boundaries and point defects influence diffusion, systematic simulations were also performed to calculate activation energy barriers for individual atomic jump paths.

A. Energy Barriers of Individual Atomic Jump Paths

To visualize detailed atomic jump paths that contributed to the increase of diffusivities, we need to first find out such paths. However, our systems involve hundreds or even thousands distinct paths not known a priori. Hence, we use an automated procedure to calculate energy
barrier of all hydrogen atoms in a chosen snapshot configuration obtained during an MD simulation. This includes the following steps: (i) a hydrogen atom is looped; (ii) this hydrogen atom is displaced sequentially in the x direction with a step size of 0.02 Å. Following each displacement, a MS simulation is performed to relax the system with the constraint that the hydrogen atom does not move in the x direction but can move freely on the plane normal to the x direction. This method is effective to find the lowest energy path unless such a path is perpendicular to x. This is not a problem because we can repeat the same procedure in the y and z directions. If the minimum energy path is not perpendicular to any of the x, y, and z directions, then the values obtained in the three directions are close. Furthermore, considering that ± directions are not symmetric in our systems due to the presence of defects, we calculated six energy barriers for each hydrogen atom corresponding to displacement in the ±x, ±y, and ±z directions. Note that this method cannot be used to distinguish the in-plane and out-plane diffusions regardless the direction of the displacement because it always converges to the lower energy path of the in-plane and out-plane diffusion.

The procedure described above was used to calculate energy barriers. For each distinct scenario (combination of grain boundary and point defect), we analyse only one snapshot configuration obtained at 110 ns of MD simulation. For each snapshot configuration, we only calculate energy barriers for 10 hydrogen atoms that are the closest to the grain boundary. The results of the calculations are summarized in Fig. 11. Although our method was automated and could therefore more exhaustively analyse the data, Fig. 11 already includes sufficient data for an understanding of relevant statistics.
Fig. 11 Statistic distribution of activation energy barriers of hydrogen diffusion near various grain boundaries, obtained from MS calculations.

Fig. 11 indicates that for the single crystal without any point defects, i.e., the $\Sigma$1-perf. case, the energy barriers reduce essentially to a single point, consistent with a single jump path (from octahedral to tetrahedral sites or vice versa). The $\Sigma$3 boundary without any point defects, the $\Sigma$3-perf. case, behaves similarly as the energy barriers reduce to almost a single point whose value is close to that in the $\Sigma$1-perf. case. The presence of point defects causes the energy barriers to spread into a large range especially for the cases of interstitials on the $\Sigma$3b boundary ($\Sigma$3b-inter.), interstitials on the $\Sigma$5 boundary ($\Sigma$5-inter.), vacancies on the $\Sigma$5 boundary ($\Sigma$5-v.), and interstitials on the $\Sigma$11 boundary ($\Sigma$11-inter.). Some jump paths in the spread have energy barriers higher than that of the perfect single crystal ($\Sigma$1-perf.), however, many paths have lower activation energies. We can therefore conclude that combined grain boundaries and point defects can cause significant increases in the overall diffusivities because there are many lower barrier paths present in such systems.

We can now select some lower energy barrier points marked in red in Fig. 11, and visualize the atomic jump process in detail to understand mechanisms of energy barrier reduction.
B. *Visualization of Low Barrier Atomic Jump Processes*

Hydrogen diffusion in single crystals is first examined. Atomic jump processes corresponding to the three red data points for the $\Sigma 1$-perf., $\Sigma 1$-inter., and $\Sigma 1$-va cases are shown respectively in Figs. 12(a) – 12(c), where yellow balls represent nickel atoms, small brown balls are background hydrogen atoms, and large red balls show the initial and saddle points of the jumping hydrogen atom with the arrow indicating the jumping direction. It can be seen from Fig. 12(a) that when the single crystal does not contain any point defects, the hydrogen atom jumped from an initial octahedral site to a neighbouring tetrahedral site with an activation energy barrier of 0.46 eV. This matches well with the value determined from the MD simulations as shown in Table II. For the chosen jump paths examined, the energy barrier was reduced to 0.44 eV when nickel interstitials were present, and to 0.42 eV when nickel vacancies were present. The jumping path was still from an octahedral site to a neighbouring tetrahedral site. However, there was an interstitial and a vacancy near the jump atom in Figs. 12(b) and 12(c) respectively as indicated by the black circle. Hence, it is the local interstitial and vacancy that caused the reduction of the energy barrier.

![Initial and saddle points of the jumping hydrogen atoms in single crystalline nickel.](image)

**Fig. 12** Initial and saddle points of the jumping hydrogen atoms in single crystalline nickel. (a) no point defects, (b) interstitials, and (c) vacancies. Note that the activation energy $Q_\alpha$ ($\alpha = x, y, z$) was obtained from MS simulations where the jumping atom was marched in the $\alpha$ direction.
Hydrogen diffusion on $\Sigma 3\{111\}$ boundary is next explored. Atomic jump processes corresponding to the three red data points for the $\Sigma 3$-perf., $\Sigma 3a$-inter., and $\Sigma 3b$-inter. cases are shown respectively in Figs. 13(a) – 13(c). Again, yellow balls represent nickel atoms, small brown balls are background hydrogen atoms, and large red balls show the initial and saddle points of the jumping hydrogen atom with the arrow indicating the jumping direction. Here the $\Sigma 3$-va. case is not shown because the diffusions with and without vacancies are similar. Instead, the $\Sigma 3a$-inter. and $\Sigma 3b$-inter. cases are compared because interstitials caused different reconstructions of the grain boundary and therefore different diffusion behaviours. It can be seen from Fig. 13(a) that in the absence of any point defects, the hydrogen atom jumped from an initial octahedral site to a neighbouring tetrahedral site as if it was in a single crystal. The activation energy barrier of this process was 0.45 eV, close to the 0.46 eV found in Fig. 12 for single crystal.

![Initial and saddle points of the jumping hydrogen atoms on a $\Sigma 3\{111\}$ grain boundary.](image)

Fig. 13  Initial and saddle points of the jumping hydrogen atoms on a $\Sigma 3\{111\}$ grain boundary. (a) no point defects, (b) interstitials with the 300 K reconstruction, and (c) interstitials with the 500 K reconstruction. Note that the activation energy $Q_\alpha$ ($\alpha = x, y, z$) was obtained from MS simulations where the jumping atom was marched in the $\alpha$ direction.
Fig. 13(b) indicates that for the selected jump path in the Σ3a-inter. case, the activation energy barrier was reduced to 0.38 eV. Furthermore, there were local nickel interstitials near the jump hydrogen atom as indicated by the oval. These interstitials also change the environment of the destination “tetrahedral” site of the jumping hydrogen atom. Hence, we can conclude that the local interstitials were responsible for the reduction of the energy barrier.

Fig. 13(c) indicates that for the chosen jump path in the Σ3b-inter. case, the activation energy barrier was significantly reduced to 0.18 eV. Interestingly, no local interstitials can be found in Fig. 13(c). However, the top layer (occupied mainly by the blue atoms) contains five extra nickel atoms. These five nickel interstitials are homogeneously distributed in the layer, causing the layer to have a shear deformation as compared to the configurations shown in Figs. 13(a) and 13(b). This shear deformation changes the atomic jump path. Hence, it can be concluded the stress and the shear deformation associated with homogeneously distributed nickel interstitials were responsible for the reduction of the energy barrier.

Hydrogen diffusion on Σ5{100} boundary is also studied. Atomic jump processes corresponding to the three red data points for the Σ5-perf., Σ5-inter., and Σ5-va. cases are shown respectively in Figs. 14(a) – 14(c). Again, yellow balls represent nickel atoms, small brown balls are background hydrogen atoms, and large red balls show the initial and saddle points of the jumping hydrogen atom with the arrow indicating the jumping direction. It can be seen from Fig. 14(a) that in the absence of any point defects, the initial and final sites of a jumping hydrogen atom cannot be clearly defined as octahedral and tetrahedral sites. However, the energy barrier is 0.45 eV, close to the single crystal case. For the chosen paths examined, the energy barrier reduced to 0.18 eV with nickel interstitials in Fig. 14(b), and to 0.30 eV with nickel vacancies in Fig. 14(c). No clear interstitials and vacancies are seen near the jumping atom, but the reduced
energy barriers can be attributed to the local lattice distortion caused by interstitials and vacancies, which can be clearly seen in Figs. 14(b) and 14(c).

Fig. 14  Initial and saddle points of the jumping hydrogen atoms on a $\Sigma 5\{100\}$ grain boundary. (a) no point defects, (b) interstitials, and (c) vacancies. Note that the activation energy $Q_\alpha (\alpha = x, y, z)$ was obtained from MS simulations where the jumping atom was marched in the $\alpha$ direction.

Finally, jump processes of hydrogen on $\Sigma 11\{311\}$ boundary is visualized. Examples of atomic jump processes corresponding to the three red data points for the $\Sigma 11$-perf., $\Sigma 11$-inter., and $\Sigma 11$-va. cases are shown respectively in Figs. 15(a) – 15(c) using the same scheme as used above. It can be seen from Fig. 15(a) that in the absence of any point defects, the chosen jump displayed had an energy barrier of 0.54 eV, which was different from the other grain boundaries explored above. Furthermore, Fig. 11 indicates that unlike the other grain boundaries where activation energy barriers were concentrated around a single point when no point defects were present, the barriers on the $\Sigma 11\{311\}$ boundary spread into a wide range. Hence, multiple distinct diffusion paths were activated on the $\Sigma 11\{311\}$ boundary. For the chosen paths examined, the energy
barrier reduced to 0.40 eV with nickel interstitials in Fig. 15(b), and to 0.13 eV with nickel vacancies in Fig. 15(c). Near the jumping atoms, interstitials are observed in Fig. 15(b) and vacancies are observed in Fig. 15(c) as shown by the ovals. These suggest that the reduced barriers were caused by these local point defects.

![Fig. 15](attachment:fig15.png)

**Fig. 15** Initial and saddle points of the jumping hydrogen atoms on a $\Sigma 11\{311\}$ grain boundary. (a) no point defects, (b) interstitials, and (c) vacancies. Note that the activation energy $Q_\alpha (\alpha = x, y, z)$ was obtained from MS simulations where the jumping atom was marched in the $\alpha$ direction.

V. CONCLUSIONS

Molecular dynamics simulations have been used to study the effects of three grain boundaries ($\Sigma 3\{111\}$, $\Sigma 5\{100\}$, and $\Sigma 11\{311\}$) and three irradiated point defects (interstitials, vacancies, and Frenkel pairs) on hydrogen diffusion in nickel crystals. The following conclusions have obtained:

1. With sufficient computing resources, extremely long molecular dynamics simulations can be used to derive Arrhenius plots of hydrogen diffusion with small statistical errors. The activation energy barriers obtained from these Arrhenius plots accounts for all possible atomic jump paths that cannot be addressed using the nudged elastic band methods;
2. For single crystals, 0.5% interstitials cause hydrogen diffusivity to increase to 2.6 times at 300 K and to 1.5 times at 600 K as compared to defect-free sample. A similar concentration of vacancies does not change diffusivities significantly;

3. $\Sigma 3\{111\}$ grain boundary does not have significant effects on diffusivities except when interstitials are present;

4. $\Sigma 5\{100\}$ grain boundary enhances the in-plane H diffusion but reduces the out-plane diffusion due to a trapping effect. Similar phenomenon is observed on the $\Sigma 11\{311\}$ grain boundary, albeit the enhancement of the in-plane diffusion is less significant;

5. Frenkel pairs do not increase diffusivities as significantly as interstitials. This is because some interstitials and vacancies annihilate, resulting in an effective reduction of interstitial density;

6. Combination of grain boundaries and point defects can have much larger effects in increasing hydrogen diffusivities than grain boundaries or point defects alone. For instance, while the $\Sigma 3\{111\}$ grain boundary has almost no effect, the diffusivity obtained with combined $\Sigma 3\{111\}$ grain boundary and homogeneously segregated interstitials is significantly higher than that with interstitials alone. Likewise, while vacancy has almost no effect, the diffusivity obtained with combined segregated vacancies and $\Sigma 5\{100\}$ grain boundary is significantly higher than that with the grain boundary alone;

7. Point defects create many distinct jump paths near grain boundaries. These paths have energy barriers spanning a wide range. The overall reduction of the diffusion energy barriers comes from the jump paths that have very low energy barriers. These low barriers are either caused by local point defects near the jumping atom, or the overall change of the grain boundary structures by the point defects segregated near the grain boundary.
Finally, we point out that the point defects studied in the present work are ideal, which behave differently from those created during irradiation cascade. We also expect differences for other fcc materials such as austenitic stainless steels as compared to nickel. Diffusion of hydrogen in austenitic stainless steels, and the effects of cascade, are a topic to be explored in a separate paper.

VI. CONFLICTS OF INTEREST

There are no conflicts of interest to declare.

VII. ACKNOWLEDGEMENTS

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