

Hydrogen enhanced dislocation cross-slip in polycrystalline nickel

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Hydrogen embrittlement (HE), degradation of the mechanical properties of metals due to the presence of hydrogen, is a persistent problem that has been attracting the attention of the material science community for about fifteen decades. Extensive experimental observations indicate the presence of nanovoids and the increase of free volume at the grain boundaries in hydrogen contaminated metals. This rate-dependent phenomenon motivates theoretical investigations of the underlying mechanisms. Here, a hydrogen enhanced cross-slip (HECS) mechanism in the close vicinity of the grain boundaries is demonstrated by direct molecular dynamics simulations and theoretical calculations. To this end, the interaction of screw dislocations with a variety of symmetric tilt grain boundaries in H-charged and H-free bicrystalline nickel is examined. The presence of segregated H atoms at the grain boundaries induces a stress field in their vicinity, and thus, the barrier for cross-slip of screw dislocations considerably decreases. The enhanced cross-slip of dislocations facilitates the formation of jogs on bowed-out dislocations. These jogs can form vacancies during the glide process. This mechanism of defect production shows nanoscale evidence of enhanced vacancy formation and subsequent increase in the free volume along the grain boundaries in the presence of H.

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I. INTRODUCTION

The fact that interstitial hydrogen degrades the mechanical properties of host metals is well established for more than 15 decades [1]. Hydrogen embrittlement (HE) is one of the most significant detrimental effects on metals such as steels and nickel based alloys [2–6]. Among many proposed mechanisms, there are a few well-known mechanisms in the literature that explain specific features of HE by focusing on particular aspects of the material response to H contamination. The mechanism of hydrogen enhanced decohesion (HEDE), for example, states that H in interfaces reduces the formation energy of open crack surfaces, and thus, makes brittle cleavage easier than other ductile failure processes in materials [7–12]. However, direct atomistic simulations of plastic deformation in the crack tip region indicate that the processes at the atomic scale are not fully captured by a thermodynamic description such as HEDE theory, since the effects of H on the rival ductile processes are neglected [13]. Experimental observations of local plastic activities in hydrogen-rich regions are the basis of the hydrogen enhanced local plasticity (HELP) mechanism [14–16]. It assumes that the presence of H alleviates the dislocation-dislocation interactions and increases their mobility. Consequently, HELP

happens in critical regions, and the material fails because its plastic capacity is exhausted. This theory is not predictive, and atomistic simulations [17,18] do not support its assumptions. The concept of nanohydride formation (NHF) is another approach to explain HE due to suppression of plastic activities in crack tip regions by the accumulation of H atoms and the formation of nanohydride regions [19,20]. This theory has quantitative success in the prediction of experimental results at room temperature [20]. More recently, a theory combining aspects of both HEDE and NHF proposed that the formation of three-layered local hydrides ahead of crack tips can embrittle nickel by blocking dislocation emission and providing enough H atoms for sufficient reduction of the surface energy [21]. The predictions of this theory, which are independent of the material's microstructure, are in reasonable agreement with experimental results. Its extension to high-entropy alloys and fcc steels has also been successful in predicting hydrogen embrittlement in these materials [22].

The present paper is devoted to clarifying the mechanism underlying experimental observations that show an enhanced propensity of nanovoid formation along grain boundaries (GBs) in H-charged nickel [23–25] as a subset of the experiments in which embrittlement is observed. In particular, Lawrence *et al.* [23] observed an inverse relationship between the amount of the free volume measured by positron annihilation spectroscopy and the grain size in polycrystalline nickel. This observation suggests that the presence of nanovoids is more pronounced in the GB regions. Moreover, Tarzi-moghadam *et al.* [25] reported enhanced damage by nanovoid formation in the presence of H in a Ni-based superalloy. The ultimate tensile engineering strain of the H-charged alloy was $\approx 15\%$. It should be noted that in the absence of hydrogen, the fracture mode in the aforementioned alloy is ductile. However,

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this mode of fracture, which is associated with void formation and coalescence, occurs at substantially higher engineering tensile strain level ($\approx 45\%$). The creation of the nanovoids in the presence of hydrogen is also observed in bcc iron. Neeraj *et al.* [26] observed dimples in the conjugate faces of a crack in H-charged α -iron. The existence of these dimples, which are remnants of the nanovoids of radius $\approx 100\text{--}200$ Å cut by the crack, suggests that the presence of H atoms facilitates the production of nanovoids in regions ahead of the crack tip, and then the coalescence of the voids gives rise to fracture and crack propagation.

Quantum mechanical calculations based on density functional theory (DFT) show that H atoms can bind to vacancies and reduce their formation energy [27,28]. However, the pure energetic calculations are not sufficient for capturing nanovoid formation. The mechanism of the production of the *additional* vacancies, and the kinetics of this process should be clarified. Li *et al.* [29] proposed a mechanism in which hydrogen not only reduces the vacancy (V_a) formation energy by binding to them, i.e., the formation of VaH_n , $n \geq 1$, complexes, but also stabilizes these defects against the usual vacancy absorption processes during plastic activities. Thus the concentration of VaH_n complexes increases, and eventually, nanovoids form by the coalescence of the complexes. However, the number of VaH_n complexes needed for the formation of a nanovoid scales with R^3 , where R is the nanovoid radius, but the surface sites of the nanovoid scale with R^2 . Thus the coalescence of VaH_n complexes in bulk will lead to the diffusion of H atoms back into the bulk. This process is not energetically favorable. Moreover, we previously showed that the presence of H atoms in VaH_n complexes does not stabilize the complex against jog formation processes in bcc iron [30] due to the high formation energy of single vacancies. Moreover, the barrier for the diffusion of the VaH_n complexes is in the range of 0.6 eV, which is not significantly lower than such barriers for single vacancies. Thus it is reasonable to assume that a vacancy formation mechanism, by which more vacancies are *produced* in the *close* neighborhood of the GBs and are attracted to it, can be responsible for the presence of nanovoids or the development of free volume in H-charged GBs. In such a mechanism, H is causing the vacancy formation but does not need to be incorporated into the vacancy, in contrast to the stabilization of bulk vacancies by H and their diffusion.

A well-known vacancy production mechanism is the drag of the jogged screw dislocations [31]. These jogs form when the screw dislocation overcomes obstacles against glide. Cross-slip is a mechanism in which screw dislocations change their glide planes. This atomic-scale plasticity mechanism attracted a huge amount of research during the past decades [32].

It is usually believed that H atoms reduce the propensity of a material toward cross-slip by segregating to the partial dislocations and the stacking fault. For example, Ferreira *et al.* [33] showed that hydrogen hinders the cross-slip of dislocations in bulk aluminum in the absence of grain boundaries. This phenomenon is likely due to pinning of partial dislocations or reduction of stacking fault energies by H atom. There are a limited number of works in the literature that studied this direct impact of H on cross-slip using simulations. Tang *et al.* [34,35] simulated the interaction of a H atom with stacking

faults in nickel. Their results based on a specific embedded atom method (EAM) potential indicate a slightly attractive interaction between the H atoms and the stacking fault, which leads to a slight reduction of the stacking fault energy. Moreover, they found that the core of the partial dislocations can act as a trap for H atoms. They concluded that depending on the location of the segregation sites, H atoms could have both an enhancing/hindering effect on the cross-slip. However, there are recent experimental observations that suggest that H atoms can increase the propensity of cross-slip. For example, Harris *et al.* [36] observed an H induced increased rate of dislocation annihilation in the precipitate hardened Ni-based superalloy Monel K-500.

Kuykendall *et al.* [37] proposed a model that describes the effect of stress fields on the cross-slip barrier in nickel. They showed that stress fields can significantly reduce this barrier. This reduction is mainly due to the Escaig stress at the glide plane, which controls the distance between the partial dislocations and makes the formation of the constrictions easier. The work of Esteban-Manzanares *et al.* [38] observes a similar trend in Al. The effect of segregated H-induced stresses on dislocation-GB interactions was previously demonstrated in Ref. [39], where the presence of hydrogen at the GB generally increased the critical shear stress for dislocation-GB interaction. Here, we demonstrate by molecular dynamics (MD) simulations that this model can explain the enhancement of cross-slip in regions a few nanometers away from H-loaded GBs. We believe that this effect is the source of an enhanced vacancy production and void formation next to GBs.

We use large-scale atomistic simulations based on an EAM potential [40,41] to demonstrate the effect of the H-induced stress fields on the reduction of the barrier for cross-slipping of screw dislocations in nickel. This potential is widely used for modeling H interactions [21,41,42] and does not exhibit spurious H clustering in nickel. We observe an enhancing effect of H-atoms at GBs on cross-slip in the cases of $\Sigma 33a$, $\Sigma 33b$, $\Sigma 41$, and $\Sigma 9$ boundaries, which represent diverse regions of the GB structural domain. In the case of the $\Sigma 33a$ GB, the emission of divacancies following dislocation cross-slip near the GB is evident within the time span of a few nanoseconds. These results are in accordance with the experimental results of Harris *et al.* [36]. The cross-slip process helps the dislocation segments to overcome obstacles against glide by changing glide planes. Interestingly, the cross-slipped segments constitute barriers for the glide of the other segments along the original glide plane. These cross-slipped segments act as new pinning points. The interplay between the applied load, the cross-slipped segments, and the segments on the original plane results in the formation of jogs and the emission of divacancies from the bowed-out dislocation, which are not purely screw dislocations any more. This mechanism of defect induced defect production explains thus an indirect impact of H on cross-slip as a source for the large vacancy and void concentration specifically observed in H-loaded metals near GBs in the experiments. This mechanism, which is mainly concerned with the mechanical effects of H through its stress field at the GBs, complements other studies on the direct chemical effects of H on vacancy cluster stabilization [43] and on the fracture energy reduction [41]. The remainder of this paper is organized as follows. In Sec. II, the theory of

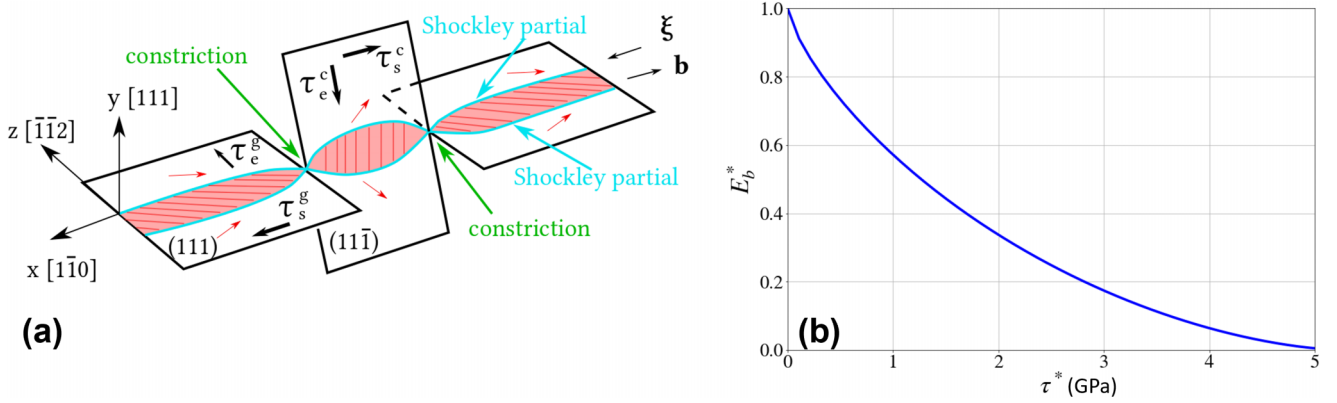


FIG. 1. (a) Schematic diagram of the FE model describing the cross-slip of screw dislocations in fcc metals. (b) Variation of the energy barrier for cross-slip of screw dislocations in terms of the effective stress of Eq. (2), as given in the work of Kuykendall *et al.* [37].

cross-slip is reviewed, and the stress dependence of the energy barrier associated with it is presented. In Sec. III, the details of atomistic simulations of dislocation and GB interactions, which lead to cross-slip of the screw dislocations, are presented. Section IV presents the results of the simulations, and a discussion on the implications of the hydrogen enhanced cross-slip mechanism and its effects on the HE process is provided in Sec. V. A summary of our findings is given in Sec. VI.

II. THEORETICAL FRAMEWORK

A well-established mechanism describing cross-slip in fcc metals is the Friedel-Escaig (FE) model [44,45]. The screw dislocations in fcc metals dissociate into two Shockley partial dislocations on the (111) glide plane, as shown in Fig. 1(a). The distance between these two Shockley partials is determined by the equilibrium of their elastic interaction energy and the energy of the stacking fault forming between them. According to the FE model, the initial step for cross-slip is the formation of a constriction, i.e., a combined partial dislocation consisting of two previously distant partial dislocations in the glide plane. Then the constriction expands into a pair of constrictions, and the dislocation segment between the constrictions changes its glide plane to the $(\bar{1}\bar{1}\bar{1})$ plane, namely, the cross-slip plane. The double constriction expands on the cross-slip plane, and the length of the cross-slipped segment increases until the whole dislocation changes its glide plane. The energy barrier associated with the cross-slip is directly related to the separation distance between the partials. Thus an external stress has a direct effect on the magnitude of the energy barriers. The resolved shear on the glide plane of the dislocation can be decoupled into two types of shear stresses based on their interaction with the partial dislocations. The Escaig stress, τ_e , is the component of the shear that changes the separation distance of the partials. In other words, by application of τ_e , initially straight partial dislocations remain straight, but their distance changes. On the other hand, the Schmid stress τ_s dictates the curvature of the partial dislocations. The same definition holds for τ_e , and τ_s on the cross-slip plane. The aforementioned shear stresses on both glide and cross-slip planes are shown in Fig. 1(a).

Kuykendall *et al.* [37] estimated the dependence of the energy barrier for the cross-slip on the applied stress in pure nickel using

$$E_b^* = \frac{E_b}{E_b^0} = \left(1 - \left(\frac{\tau^*}{\tau_0}\right)^p\right)^q, \quad (1)$$

$$\tau^* = c_e^g \tau_e^g + c_e^c \tau_e^c + (D_s^c \tau_s^c)^2, \quad (2)$$

where E_b , E_b^0 , E_b^* , are the cross-slip energy barrier and the stress-free cross-slip energy barrier in bulk, both obtained from atomistic simulations, and the normalized cross-slip energy barrier, respectively. τ^* is the effective shear. The numerical values for the parameters of this model are $E_b^0 = 2.194$ eV, $c_e^g = -1.781$, $c_e^c = 0.9332$, $D_s^c = 0.6788 \text{ GPa}^{-\frac{1}{2}}$, $\tau_0 = 5.275$ GPa, $p = 0.7453$, and $q = 1.636$. The subscripts s and e denote the Schmid and Escaig stresses, and the superscripts g and c correspond to glide and cross-slip planes, respectively. This formulation is based on fitting the results of the simulations of the cross-slip in pure nickel for different stress states and there is no physical motivation beyond this fitting function. Particularly, in the regions where τ^* exceeds 5.275 GPa, this formulation gives rise to nonphysical complex values for the barrier. It should be noted that these simulations were done using a certain EAM potential developed by the authors. However, for the following discussion, we are not concerned with the quantitative predictions of this formulation. The purpose of using this formulation is to demonstrate the effect of stress induced by the H atoms around the GBs on the magnitude of E_b . Figure 1(b) shows the variation of E_b^* versus the effective stress, τ^* . It can be seen that E_b^* decreases to below 0.33 when the effective stress is increased to values more than 2.0 GPa. This barrier corresponds to the rate of 10^8 s^{-1} in nickel calculated using the Arrhenius law in conjunction with nickel's Debye frequency. Note that this magnitude of stress cannot be reached in defect-free bulk of the material due to the plastic activities, but it is achievable in the close vicinity of defects such as GBs in which the atomic distortions are high.

III. SIMULATION DETAILS

This section has two separate parts. At first, we give the details of the molecular static simulations used to compute

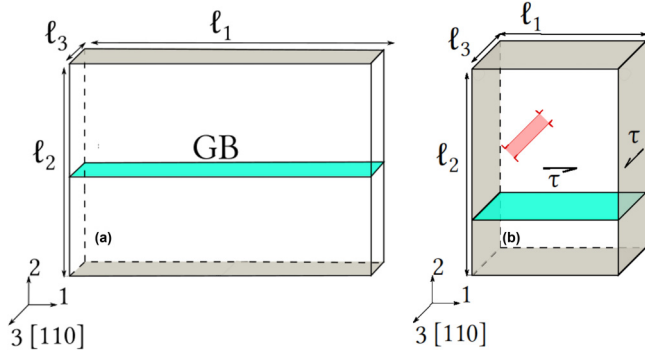


FIG. 2. Schematic representation of the simulation cells used for (a) attaining the stress field introduced by a GB and (b) simulating the cross-slip of screw dislocations (red) near the GB (green). The tilt axis of all of the GBs considered in these simulations is along $x_3 = [110]$, whereas the other axes are GB-dependent. The free surfaces are indicated by a grey shading, and the other boundaries are periodic.

the stress state around selected types of GBs covered by hydrogen for known chemical potentials. In the second part, the details of the MD simulation used to derive the interaction between screw dislocations and the stress field of H-loaded GBs are given. The molecular statics and dynamics simulations are performed using the Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS) [46]. Atomic configurations are visualized using the Open Visualization Tool (OVITO) [47].

A. Computation of the stress state along symmetric tilt grain boundaries in nickel

We start by computing for representative GBs the stress field induced by segregated H atoms. We focus on symmetric tilt GBs with the tilt axis $\langle 110 \rangle$. The fcc slip plane $\{111\}$ contains this tilt axis. The reason for this choice is that the simulation of asymmetric tilt boundaries interaction with dislocations under applied stress is challenging due to their complicated stress state even under simple loading modes. Having the tilt axis on the slip plane enables us to simulate straight screw dislocations in periodic specimens. We construct simulation cells of size $\ell_1 \times \ell_2 \times \ell_3 \sim 1080 \text{ \AA} \times 1000 \text{ \AA} \times 9.6 \text{ \AA}$. Each supercell contains an instance of GB (Ni $\Sigma 9(221)\langle 110 \rangle$, $\Sigma 33a(441)\langle 110 \rangle$, $\Sigma 33b(554)\langle 110 \rangle$, or $\Sigma 41(443)\langle 110 \rangle$) at the central plane $x_2 = 0$ as shown in Fig. 2 a. Note that $\langle klm \rangle$ denotes the family of directions crystallographically that are equivalent to $[klm]$. We chose the cell size to be large along the x_1 axis to capture the stochastic effects due to fluctuations in the local environment and concentration of the segregated H atoms along the GBs.

The simulation cells are periodic in x_1 and x_3 directions and have free boundaries in the x_2 direction. We note that GBs, even without H atoms, have an intrinsic stress field. In a finite-size sample that is fully relaxed to zero net stress in all directions, this intrinsic GB stress is balanced by a compensating stress in the two grains on either side of the boundary. This compensating stress decreases with increasing the sample size and would vanish in the limit of significantly large grains.

We fix the width ℓ_1 of the sample to an integer multiple of the periodic large distance along x_1 to mimic significantly large grains. The periodic distances are calculated based on the defect-free Ni lattice constant at 300 K. Thus the Ni atoms in the grains far from the GB are under zero stress, while the GB stress is equal to the stress of the same GB embedded in an infinitely extended bulk. The simulation box is relaxed using the conjugate gradient method [48] by setting the force tolerance to $10^{-5} \text{ eV/\AA}$.

For hydrogen charged samples, the bulk concentration is given by

$$c_0 = e^{-E_f^{\text{bulk}}/k_B T}, \quad (3)$$

where E_f^{bulk} is the formation energy of the H atom in bulk nickel at a given chemical potential μ_H (i.e., $E_f^{\text{bulk}} = E_{\text{bulk}}^{\text{1H}} - E_{\text{bulk}} - \mu_H$) and k_B and T are Boltzmann's constant and temperature, respectively. The formation energy of the H atom at $\mu_H = 0$ is $E_{\text{for}}^0 = E_{\text{bulk}}^{\text{1H}} - E_{\text{bulk}}$. The concentration of H atoms at each binding site of the GBs is calculated as [49]

$$c_i = \frac{1}{1 + c_0^{-1} e^{\Delta E_i/k_B T}}. \quad (4)$$

Here, ΔE_i is the segregation energy of the H atom at site i , $\Delta E_i = (E_{\text{GB}}^{\text{1H}} - E_{\text{GB}}) - (E_{\text{bulk}}^{\text{1H}} - E_{\text{bulk}})$. These concentrations c_i are used for preparing the simulation specimens, as described in the next section. In this work, we chose the temperature to be room temperature and the background concentration to be $c_0 = 0.001$ (i.e., 1000 at. ppm), which is equivalent to a *relative* chemical potential $\mu'_H = \mu_H - E_{\text{for}}^0 = k_B T \ln c_0 = -0.17 \text{ eV}$ at 300 K. This concentration is close to the experimental levels at which hydrogen embrittlement in nickel has been observed [3,50]. The segregation energies and binding sites are attained using the EAM potential based on the Angelo *et al.* [40,51] potential, and improved by Tehranchi and Curtin [41] to describe the segregation energies of H at $\Sigma 5(210)\langle 100 \rangle$ GB in closer agreement to those of DFT calculations of Refs. [52,53]. For the details regarding the potential and procedures for finding the binding sites, we refer to Ref. [54] in which the binding sites where the vertices of the Voronoi volumes around the nickel atoms complemented with the sites found by manual search. After saturation of the GBs at 300 K, we relax the structure using the same scheme as we use for the H-free samples described earlier in this section. We neglect the H-H interaction in the GBs because of their small magnitude (less than $\approx 10\%$) in comparison to the segregation energies. This assumption precludes the formation of the hydrides at the GBs. Formation of this hydrides can be investigated using molecular dynamics–Monte Carlo (MD-MC) simulations as is done in Ref. [55].

The segregation energies of H atoms at the different sites of the GBs of interest are given in Ref. [54]. Using these segregation energies in Eq. (4) at room temperature and for a background concentration of $c_0 = 0.001$ (i.e., 1000 at. ppm), different values for c_i can be obtained. Since the segregation energies of most grain boundary sites are between 0.15 and -0.25 eV , the typical concentration at grain boundary sites would be between 0.5 and 0.9 at room temperature. This means that the H atoms are nonuniformly distributed at the GB. To achieve the randomness, we generated a random

number between zero and one and filled the i th-type site only when this number is less or equal c_i . Since the misfit volumetric strain associated with the interstitial H is high (≈ 0.3 for bulk Ni), the distortion caused by an H atom will have an impact beyond the occupied site. The resulting interplay between sites that are occupied by H and their distorted/undistorted neighboring sites in combination with the stress of the GB will dictate the input for Eq. (2). As a consequence, τ^* at each specific site i is not only a function of the concentration c_i , but also of the concentration of its neighboring sites. The quadratic dependence of τ^* on Schmid and Escaig stresses for the different crystallographic planes adds another level of complexity. This hydrogen-induced stress field will interact to any pre-existing stress state in the vicinity of the GB, e.g., roughened GBs. In these cases, the quantification of the combined effect requires a statistical hydrogen segregation study on roughened grain boundaries clarifying the binding energies, preferred binding sites and H-coverage of many configurations.

B. Finite temperature simulation of cross-slip of screw dislocations near the GBs

We start by inserting a straight screw dislocation along the x_3 axis in a simulation box with dimensions of $\ell_1 \times \ell_2 \times \ell_3 = 236 \text{ \AA} \times 290 \text{ \AA} \times 480 \text{ \AA}$. This supercell comprises of $\approx 3 \times 10^6$ atoms. The screw dislocation is inserted using the displacement field caused by the interaction of a screw dislocation and a GB as given in Ref. [56]. The vertical separation of the dislocation and the GB plane is set to be $\sim 120 \text{ \AA}$. The simulation cell is periodic along the x_3 direction, and the other directions are free. The geometric details of the specimen are given in Fig. 2(b).

The MD simulations are performed in an NVT ensemble with a Langevin thermostat [57] using the velocity-Verlet algorithm [58] with the integration time step of 0.4 and 1 fs for the H-charged and H-free cases, respectively. The lower timestep for the H-charged simulations is a conservative measure to prevent unphysical sporadic displacements of the light H atoms. The temperature of the system is fixed at 300 K. The system is equilibrated for 200 ps using the NVT ensemble. Then, the specimen is subjected to an increasing shear stress, by application of strain increments to the atoms with magnitude of $\Delta\epsilon = \mathbf{C}^{-1}\Delta\sigma$, where $\mathbf{C}$ is the elastic stiffness tensor calculated with respect to the x_i coordinate system and

$$\Delta\sigma = \begin{pmatrix} \sigma_{11} & \sigma_{12} & \sigma_{13} \\ \sigma_{21} & \sigma_{22} & \sigma_{23} \\ \sigma_{31} & \sigma_{32} & \sigma_{33} \end{pmatrix} = \begin{pmatrix} 0 & 0 & 80 \\ 0 & 0 & 0 \\ 80 & 0 & 0 \end{pmatrix} \text{MPa}. \quad (5)$$

Loading is only increased if the dislocations have relaxed to a stable configuration, i.e., the dislocation topology does not change during 200 ps. This type of loading prevents competition between the cross-slip rate and the loading rate. This method guarantees that the different dislocation segments find their steady-state structure. This adiabatic decoupling is crucially necessary, since the loading rates in MD simulations are orders of magnitude higher than the experimental loading rates. Thus the above-mentioned competition is not physical. Appendix A demonstrates the effects of high loading rates on the simulation results.

IV. RESULTS

In this section, we present the results and the analysis of the simulations and discuss various aspects and implications of the hydrogen enhanced cross-slip process.

A. Stress state and cross-slip barrier of H-free and H-loaded symmetric tilt grain boundaries

Figure 3 illustrates the variation of the effective stress τ^* normal to the selected GBs for both H-free and H-charged cases. Figure 4 shows the variation of the estimated energy barriers, E_b , for cross-slip for both cases and in the same GBs using these data together with Eq. (1). It is evident that even in the H-free cases, the regions within 10 Å distance from the GB plane are subjected to a large effective stress. In the H-free case, the GB induced stress is periodic along x_1 direction. The periodic length is a few angstroms. In the cases of $\Sigma 9$, $\Sigma 33a$, and $\Sigma 41$ the GB contains an open structure. In the case of $\Sigma 33b$ and $\Sigma 41$ an array of partial dislocations exists (see Ref. [54]).

Loading the GBs with H, the magnitude of τ^* significantly increases in the localized regions. For the H-charged case, this increase extends up to 40 Å away from the GB planes, whereas for the H-free case, this increase is only limited to the region with a distance less than 10 Å. For $\Sigma 33b$ and $\Sigma 41$, the extension of the region is slightly less pronounced in the figure, while still clearly noticeable.

The reason for this significant increase in the regions that are at the nanometer distance from the GB plane is the Escaig stresses in Eq. (2). The Escaig stress is associated with the shear in x_1x_2 plane that increases due to the presence of the H atoms in the GB and the distortion associated with them. The comparison of the H-free and the H-charged cases in Fig. 3 also reveals that the presence of H atoms does not expand the grey region of extremely high stress ($\geq 5 \text{ GPa}$) in which the formulation collapses. The details of this effect are discussed using an elastic model in Appendix B.

Large fluctuations along the x_1 direction are observed in the H-charged samples. They originate from the statistical distribution of the H atoms at the binding sites of the GB and the structure of GB. The spatial distribution of binding sites for H atoms along the GBs also depends on its structure. For $\Sigma 9$ and $\Sigma 33a$ GBs, the most favorable binding sites (highlighted with black spheres in Fig. 3) are more uniformly distributed along the x_1 direction due to the translational symmetry of kite structures. For a more detailed depiction of the binding sites, see Fig. 2 of Ref. [54]. For $\Sigma 33b$ and $\Sigma 41$, the most favorable binding sites ($\Delta E_i < -0.15 \text{ eV}$) are located near the core of the geometrically necessary partial dislocations. Interestingly, the latter simulation gives rise to a more uniform distribution of shear stress. The reason is that the accumulation of the H atoms at the core of the dislocations mainly changes the magnitude of the distortions in those regions, while it keeps the other regions close to the one for the H-free case. Thus the presence of H only changes the magnitude of the distortion. This distortion dictates the magnitude of the effective stress, i.e., with a qualitatively similar distribution.

The stress induced by the H atoms is added to the pre-existing stress of the GB, and the resulting Schmid and Escaig

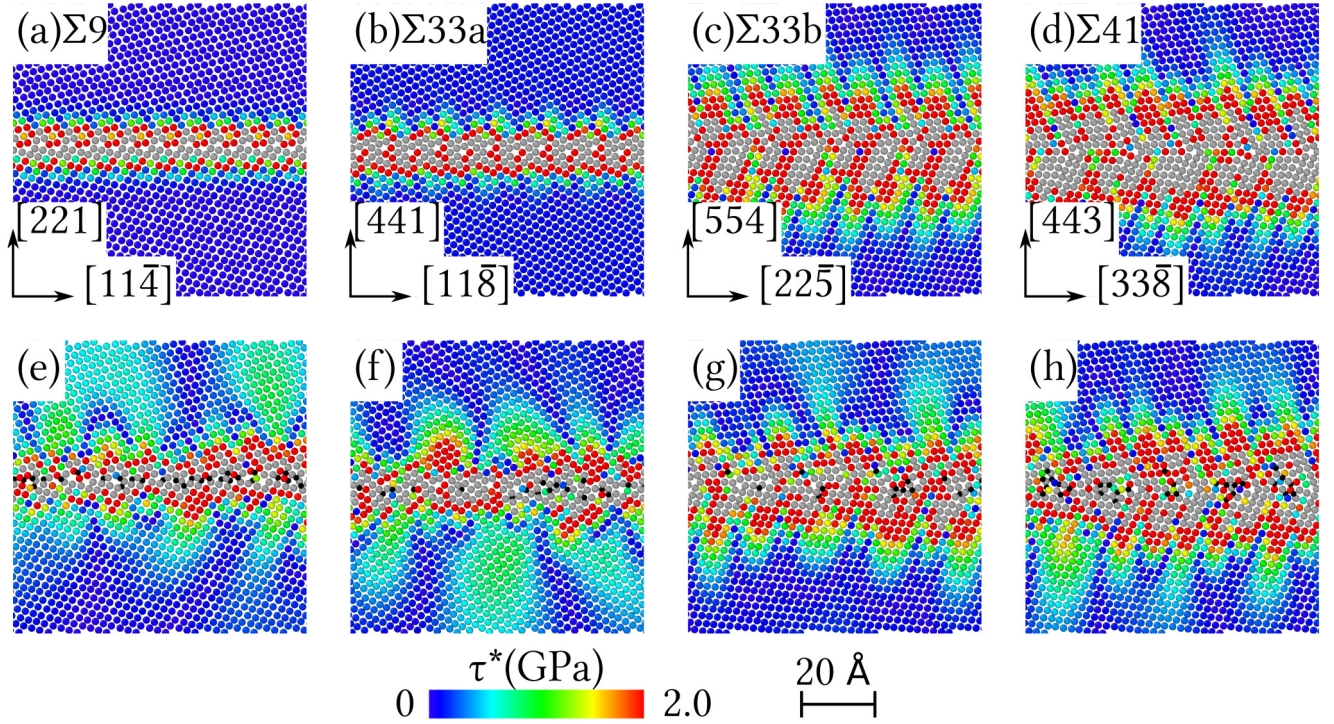


FIG. 3. The variation of the effective shear stress τ^* in the vicinity of various grain boundaries. (a)–(d) and (e)–(h) correspond to the H-free and H-charged cases, respectively. The horizontal and vertical axes in the figures are along x_1 and x_2 directions in Fig. 2(a), respectively. The H atoms are highlighted as black spheres, and the nickel atoms are color coded according to the magnitude of the effective shear stress. All Ni atoms with an effective shear of more than $\tau_0 = 5.275$ GPa at which the formulation given in Eqs. (1) and (2) breaks down are color coded as grey.

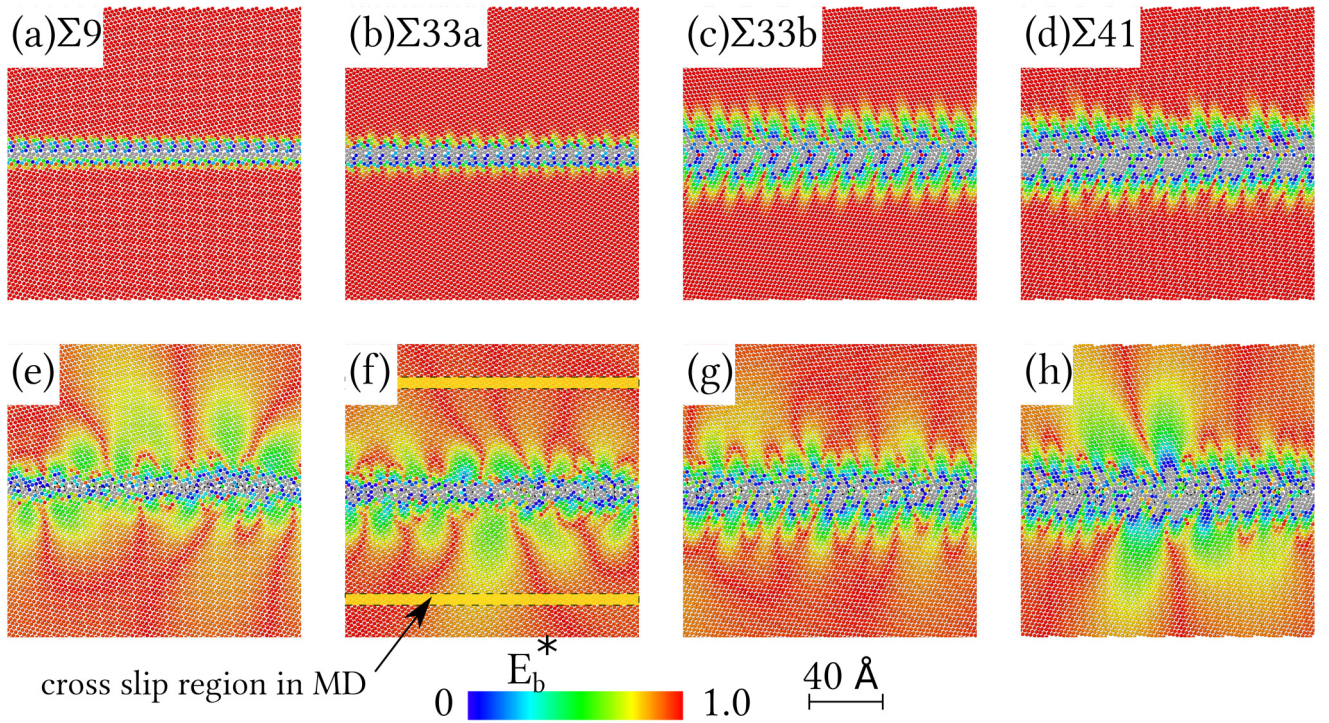


FIG. 4. Variation of the estimated energy barrier for cross-slip E_b in the vicinity of the grain boundaries shown in Fig. 3. (a)–(d) and (e)–(h) correspond to the H-free and H-charged cases, respectively. The crystallographic directions are the same as those of Fig. 3. The atoms are color coded according to the magnitude of the energy barrier. In the grey regions, the effective shear stress τ^* is above τ_0 , which results in unphysical complex values for the energy barrier of cross-slip.

stresses will enter in Eq. (2). Note that the Escaig and Schmid stresses are evaluated for two separate (111) type planes, which contain the rotation axis of the GB. These planes are the glide planes of a screw dislocation with a dislocation line parallel to the GB plane. Cross-slip happens between these two planes. These three shearing stresses are plugged into Eq. (2). Due to this combined effect, the interpretation of τ^* as a conventional stress component is misleading.

Figure 4 shows that according to Eq. (1) there are low-energy barrier regions in H-charged samples within $\approx 50\text{\AA}$ distance from the GBs. The region at which the cross-slip is observed in the MD simulations is also indicated for the case of the $\Sigma 33a$ GB by the yellow bands.

Due to the specific functional form of Eq. (1), there are regions in which the result of this equation becomes complex or infinite. The corresponding sites are color-coded in grey in Figs. 3 and 4 and do not have a physical meaning. These regions exist in both the H-free and H-charged cases, and are attached to the GB. The presence of H atoms does not increase the thickness of the grey region. Any dislocation coming from the bulk towards the GB first passes through a low barrier region and undergoes cross-slip if possible. Thus we can safely disregard the regions in which Eq. (1) gives rise to the unphysical values for the energy barrier.

The yellow bands in Fig. 4(f) show the range of distances at which we observe a cross-slip event in our MD simulations of $\Sigma 33a$ (see next section). These yellow bands are close to the low barrier regions in the simulations but far from the grey region in which the model breaks down. However, there was no cross-slip observed in the H-free samples, for which the low barrier regions are only a few Ångströms apart from the structural features of the GB. In these regions, the interaction of the dislocation and GB is more complex than what can be described by the interaction of the stress field.

In order to shed more light on the interaction between the stress field of the GB and the stress field induced by the presence of interstitial H atoms at the boundary, we construct and analyze a simple elasticity model in Appendix B in which the H atoms and the GB are modeled by inclusions and an array of dislocations, respectively. We show that even in this simple first-order approximation, the complex features that we observe in the simulations exist. This analysis is important to prove that the formation of the low barrier regions around the H-charged GBs is a rather general phenomenon and not an artifact of the simulations. Moreover, since various effects contribute to the complex variation of the energy barriers, it is important to recognize which of them dominates the underlying physics. To provide further validation for the mechanism, we deleted the H atoms in the supercells while freezing the nickel atoms at the $\Sigma 33a$ GB and repeated the barrier calculation procedure. The same results were obtained indicating that the atomic distortion in the nickel lattice causes the decrease in the barrier

B. Cross-slip of screw dislocations near H-charged symmetric tilt GBs

We now examine the effect of H-enriched GBs on the nature of their interaction with screw dislocations. To this end, we simulated the interaction of a screw dislocation with

a $\Sigma 33a$ GB in the presence and absence of hydrogen. The loading history is given in Fig. 5(a).

Selected representative configurations which we observe during the interaction of the screw dislocation and the $\Sigma 33a$ GB are given in Fig. 5 for the H-charged case. It can be seen that constrictions appear at $\tau_{\text{app}} = 80\text{ MPa}$ [$t = 0.4\text{ ns}$, Fig. 5(c)]. Subsequently, a single dislocation segment cross-slips at $\tau_{\text{app}} = 80\text{ MPa}$ ($t = 0.56\text{ ns}$). The cross-slip segments expand, but a single segment that is still at the original glide plane acts as an obstacle for the glide of the whole dislocation on the cross-slip plane. Since we do not increase the load until the dislocation becomes stable, it does not bow out. When the applied stress is increased by another 80 MPa (i.e., $\tau_{\text{app}} = 160\text{ MPa}$), the dislocation starts to bow out at $t = 0.8\text{ ns}$. Figure 5(d) shows the configuration of the dislocation and GB at $t = 2.4\text{ ns}$ in which the bow out is visible. During the bow-out process, a divacancy forms below the bow-out segment. This reaction represents an H enhanced vacancy production mechanism that happens in the slow rate regime. Eventually, the dislocation is unpinning and moves into the grain boundary at $t = 2.44\text{ ns}$ ($\tau_{\text{app}} = 320\text{ MPa}$) through the formation of a loop around the obstacle. Since in the H-free case, the dislocation enters the GB at $\tau_{\text{app}} = 80\text{ MPa}$, it is noteworthy that the HECS mechanism is hardening the material, i.e., increases the yield stress. This feature is in contrast to the HELP picture, in which H increases the local plasticity. The effect of H-induced stress fields on the critical stress for dislocation–GB interactions was preliminarily studied in Ref. [39] using a narrow simulation box along the x_3 direction. A comprehensive investigation for long dislocation segments will be a natural next step but remains beyond the scope of the current study.

C. Details of the point-defect production mechanism

Let us now focus on the atomistic process, which leads to the emission of the divacancy. Fig. 6(a) shows the process of the divacancy formation in the same simulation but from a different perspective. At $t = 1.72\text{ ns}$, we observe jogs in the dislocations. These jogs are formed by the relaxation of constrictions that develop at the curved segments of dislocations, where the character of the dislocations is no longer purely screw. It should be noted that the relatively long (4.8 nm) periodic length of the supercell minimizes the constraints on dislocation motion due to finite size effects. It is also worth noting that the barrier for the formation of constrictions is low, and the dislocation is now bowed out, with a complicated stress state. Thus the formation of jogs on segmented but curved dislocations becomes feasible. In the absence of these conditions, cross-slip of dislocations will not lead to the formation of jogs. By the formation of jogs, the stacking fault becomes stepped. We highlighted two important jogs by J_1 and J_2 . It can be seen that jogs J_1 and J_2 merge together at $t = 1.96\text{ ns}$. The resulting double jog spontaneously rearranges and forms a divacancy configuration at $t = 2.20\text{ ns}$. The applied shear stress drives the dislocation into the [112] direction, and the divacancy is left behind the dislocation. This separation process, which is schematically shown in Figs. 6(b)–6(e), is the fundamental mechanism of divacancy formation. It is triggered by the presence of H atoms in the vicinity of the GB.

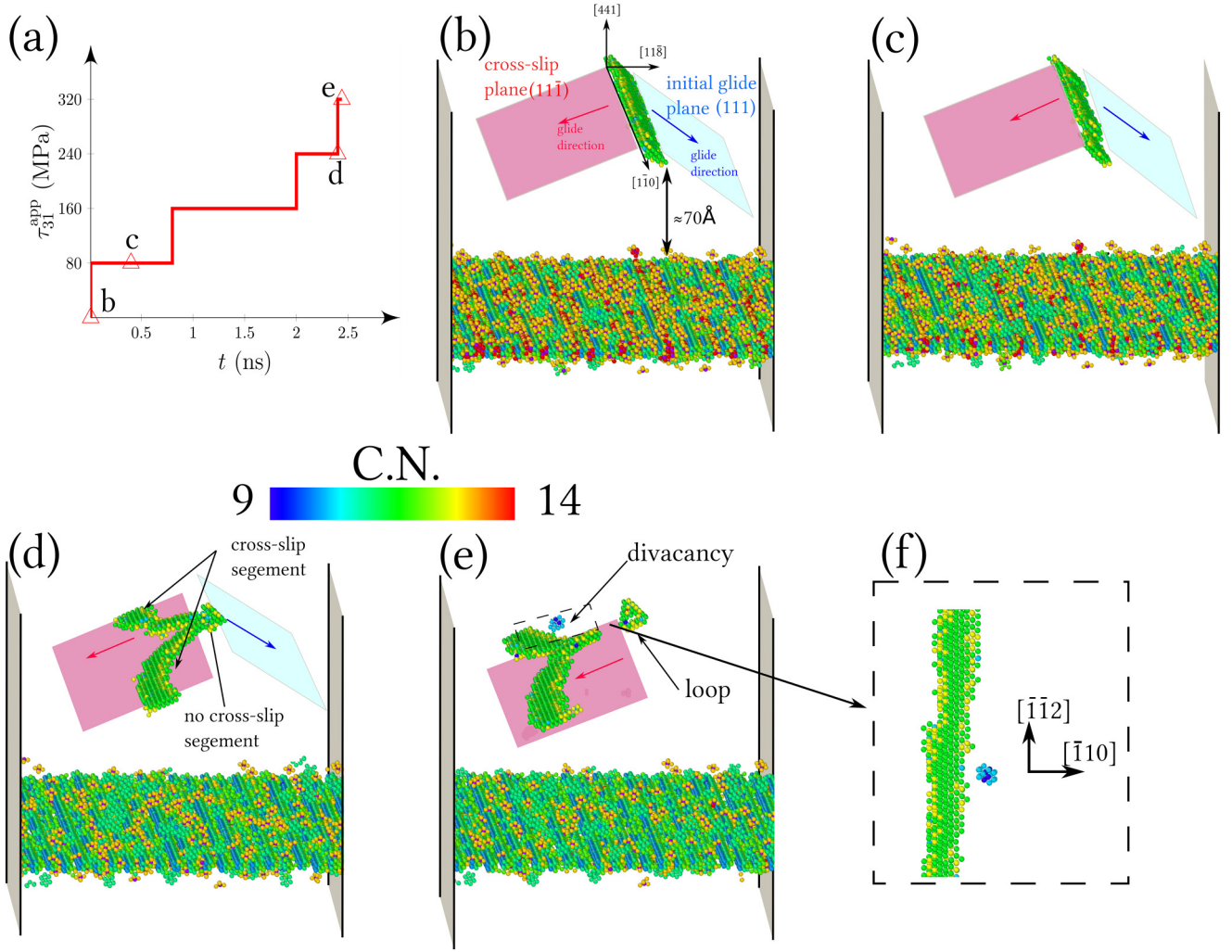


FIG. 5. (a) The time history of the applied load on the simulation box. Key configurations observed in the reaction of a screw dislocation with a H-charged $\Sigma 33a$ GB: (b) the initial configuration; (c) the formation of a constriction at $t = 0.4$ ns; (d) the cross-slipping of specific segments of the dislocation at $t = 2.40$ ns. The glide of these segments is hindered by the segments on the original glide plane. Thus the dislocation bows out. (e) The dislocation emits a divacancy and releases it from the obstacle by the formation of a loop at $t = 2.44$ ns. The H atoms are highlighted as purple spheres, and the nickel atoms at the dislocation and GB are color-coded according to their coordination number (CN). The grey planes are aligned with the corresponding simulation cell boundaries as guide to the eyes. They are not depicting the actual box size of the simulated samples, i.e., in contrast to Fig. 2(a), only a subset of the simulation box is shown. (f) Top view of the dislocation segment and the divacancy left behind it.

As shown in Fig. 5(a), additional jogs are present along the dislocation line, but are absorbed in the obstacle segment. Due to the relatively high barrier for H diffusion in nickel (≈ 0.46 eV), the segregated H atoms are located in the GB region and do not contribute to the pinning of the partial dislocations or to the stabilization of the divacancy. These jogs form due to the complex interaction between the bowed-out segments of the dislocation and the dislocation segment lying on the original glide plane. We also performed similar simulations but with different loading rates, for $\Sigma 33b$, $\Sigma 41$, and $\Sigma 9$, GBs as given in A. In all these cases, cross-slip was observed in H-charged samples, whereas in the H-free cases, we did not observe any cross-slip. In our simulations, image forces of the free surfaces perpendicular to the x_1 direction exist but since these forces are present in both H-free and H-charged cases, the overall picture does not change.

V. DISCUSSION

Our investigations demonstrate that the energy barrier for the cross-slip of screw dislocations in nickel is significantly reduced when H atoms are present at the GB due to their large stress field. This reduction becomes evident by both direct MD simulations and the empirical approximation, Eq. (1). The occurrence of cross-slip within the time scale of the MD simulations (a few ns) under relatively low applied stress fields indicates the significant reduction of this energy barrier in comparison to the barrier in bulk nickel (≈ 1.0 eV [59]). Indeed, in direct MD simulation of the H-free samples, we did not observe any cross-slip close to the GB at these timescale. Our simulations show that cross-slip occurs for the cases of $\Sigma 9$, $\Sigma 41$, $\Sigma 33a$, and $\Sigma 33b$, at 300 K and with higher rates than reported values in the literature [60] (see Appendix A)

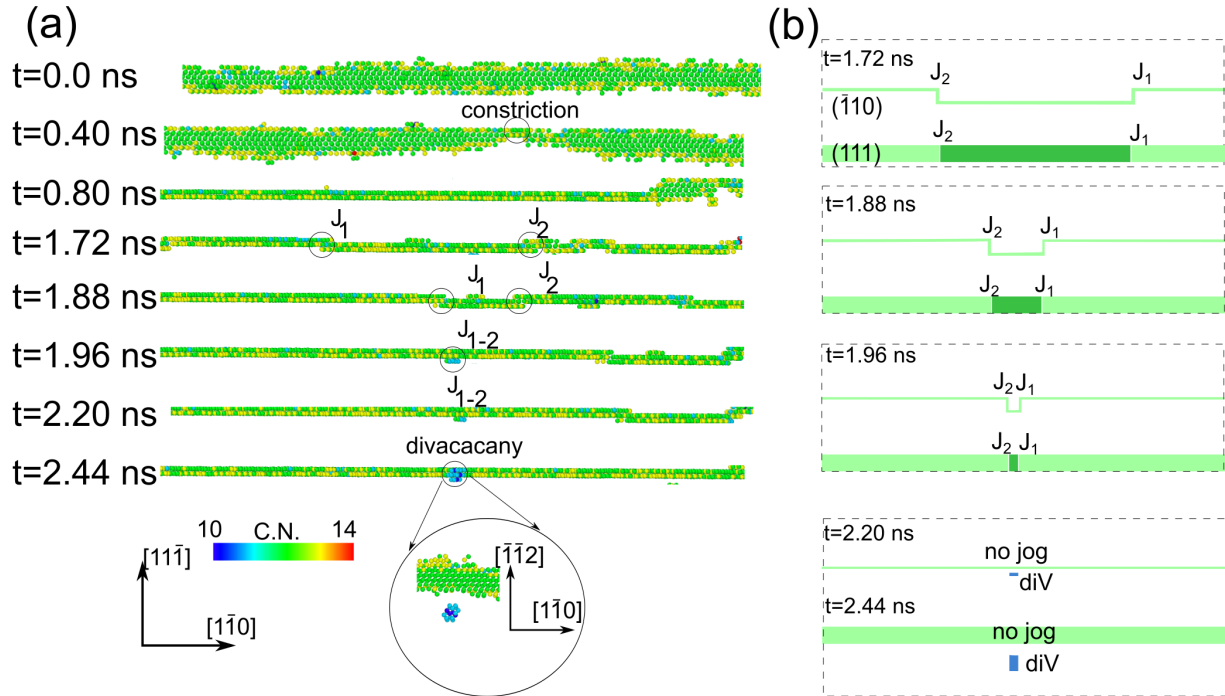


FIG. 6. (a) Snapshots of the dislocation in the MD simulation of the interaction between the $\Sigma 33a$ GB and the screw dislocation. The initial dislocation is oriented along the original glide plane ($t = 0$). At $t = 0.8$ ns several segments of the dislocation enter the cross-slip plane. Jogs J_1 and J_2 merge. After relaxation of the merged jogs a divacancy forms. The spheres denote the nickel atoms which are not fcc-bulk-like. The color-coding is due to the coordination number (CN) of these atoms (see color bar). For the last snapshot ($t = 2.44$ ns), the top view of the dislocation segment and the divacancy is given in the circle. (b) Schematic diagram of steps resulting in the formation of the divacancies. In each subfigure, the upper and lower pictures show the side and top view of the dislocation lines, respectively. The dark green dislocation segments are at the lower glide plane while the green segments are on the top one. The region depicts the atomic configuration of the di-vacancy on specific atomic planes.

clearly indicating a reduced barrier for cross-slip due to hydrogen.

It should be noted that since the barrier for the diffusion of H in bulk Ni is relatively high (≈ 0.46 eV), MD simulations cannot capture such a long-range diffusion of H toward the dislocations. However, since the hydrostatic pressure field associated with screw dislocations is effectively zero, there is no driving force for a long-range diffusion of both the H atoms and vacancies towards screw dislocations. Thus the neglect of long-range diffusion in our simulations does not undermine the validity of the conclusions made.

In the previous analysis of the MD simulations we have shown how the barrier for cross-slip is reduced by the stress field of the H-charged GBs. We note that in regions far from the GBs, the concentration of H atoms is at most a few thousand at. ppm, and thus their effect through stress on cross-slip is likely limited. We now discuss the driving force for cross-slip. In real materials, grain sizes are far larger than the size of our simulation. The image forces are not present and thus, there are two different driving forces. Firstly, the applied shear load drives the dislocation towards the GB. Secondly, and more importantly, the local stress field at damaged and H-charged GBs drives different segments of the dislocation to undergo cross-slip.

The latter driving force can have two different reasons. On the one hand, the segregated H atoms are subject to

statistical spatial fluctuations at the GB plane as described in the previous section, which induce fluctuations in the stress field near the GB and make some planes easier and some planes harder for dislocation glide. Thus the dislocation tends to change its plane from the hard glide plane to the easy ones, and this change requires cross-slip as it took place in the MD simulation. On the other hand, the plastic deformation causes accumulated damage (residual slip) in the GBs. When a dislocation enters the GB, it can dissociate, get absorbed, or be transmitted to the adjacent grain [61–63]. If it dissociates to grain boundary dislocations (GBDs), then some of these GBDs can be sessile and contribute to the accumulation of Burgers vectors at the GB. If the dislocation only gets absorbed by the boundary, its Burgers vector also accumulates at the boundary.

Given the nonuniform distribution of the residual slip at the damaged GBs, we can expect that some segments of a long screw dislocation will change their planes, and thus the driving force for cross-slip, which will be associated with the formation of jogs and constrictions will increase. These newly formed defects are then the sources for extra vacancies. In addition, it should be noted that the residual Burgers vectors are themselves traps for hydrogen and make the H distribution at the GBs more nonuniform. In the absence of H atoms, the stressed regions around the GB do not form, i.e., the barrier is not decreased. Thus, even in the case of increased

driving force, the rate of the cross-slip close to damaged GBs would not be sufficient for a significant increase in vacancy production.

Another interesting effect of the cross-slip is the induction of extra pinning against dislocation glide. Let us consider the case of $\Sigma 33a$. In the H-free case, an applied stress of 80 MPa is required to bring the dislocation into the GB. However, in the H-charged cases, constrictions already form at this applied stress, initiating the cross-slip process before the dislocation enters the GB. As shown in the simulations, segments of dislocation that cross-slipped and are consequently on the preferred glide plane will glide on that plane due to applied shear interacting with the grain boundary. However, the segments of the dislocation that did not undergo cross-slip and remain on the original glide planes cannot follow this motion on the cross-slip plane because they would be required to climb. Thus, in the absence of extensive vacancy production and diffusion, the latter segments cannot climb but act as pinning points. As a result, the former segments bow out as it is shown in Fig. 5(d). It should be noted that in the bulk of the material in which the complex interaction between the dislocations and grain boundaries is absent. In these materials, GB is absent, the bowing out of the cross-slip segment does not bow out, and the full dislocation will cross slip to the new plane.

This phenomenon leads to extra hardening and severe plastic deformations in the close vicinity of the GBs. Even after releasing the dislocation, the debris of the sessile segments remains and will act as an obstacle for the next coming dislocations. This finding, which is in contrast with the HELP picture in which H atoms facilitate local plasticity, are in accordance with the experimental observations of Lawrence *et al.* [23], who found extra hardening in polycrystalline nickel by the addition of hydrogen. The additional hardening can have different origins, but the mechanism revealed in this work can be one source for it.

The most important result of our simulations is, however, the indication of the mechanism for vacancy production near GBs. It is usually believed that H atoms stabilize vacancies formed during plastic deformation by the formation of $Va_m H_n$ clusters and that these clusters subsequently aggregate and form nanovoids [29]. However, Nazarov *et al.* [43] showed that the minimum formation energy of the VaH_n clusters in the experimentally relevant range of relative chemical potentials, i.e., $-0.20 \leq \mu'_H \leq -0.10$, is 0.90 eV corresponding to VaH_6 . Thus the bulk concentration of this cluster is $C_{VaH_6} = 2.32 \times 10^{-16}$ at room temperature. The average distance between the vacancy clusters at this concentration is $d_{av} \approx 40 \mu\text{m}$. Given the fact that the diffusion barrier for these clusters in nickel is high ≈ 2.0 eV [64], the formation of nanovoids close to GBs by coalescence of the vacancy clusters in the bulk is unlikely. However, if we consider our vacancy formation mechanism due to the enhanced cross-slip, the distance of the produced vacancies and the GB reduces to a few *nanometers*. An estimation of the rate of vacancy production due to enhanced cross-slip, which is given in Appendix C, indicates that this mechanism can produce several orders of magnitude higher concentrations of vacancies than in equilibrium. Thus the here identified production of vacancies during plastic

deformation explains void formation at GBs in H-charged nickel-based alloys in the experimentally relevant temperature and μ_H domain. The produced vacancies can diffuse to the GB which is only a few nanometers apart. There they damage it and subsequently decrease the cohesive strength of the GB. This mechanism could contribute to embrittlement, consistent with work of Tanguy [65], which shows that only densely distributed small cavities cause embrittlement. In this regard, the H atoms at the GB on one hand decrease the fracture energy due their chemical bonding on the free surfaces. On the other hand, the stress field associated with their presence at the GB leads to an excess (di)vacancy production mechanism. The fracture energy of the GB is further reduced when the (di)excess vacancies are absorbed at it. Previous studies on Ni-grain boundaries [41,54] showed that the chemical effects of segregated H atoms at the GB are insufficient to induce HE. The vacancy production mechanism identified in this study can be considered as the missing part of the HE process puzzle in nickel based alloys. Finally, it should be noted that in principle the extension of this mechanism to other fcc materials, such as Al and austenitic steel, is possible because the H are interstitial solutes and thus induce large stress fields around the GBs.

VI. CONCLUSION

In this work, we have introduced the hydrogen enhanced cross-slip (HECS) mechanism. The stress field around grain boundaries in H contaminated specimens causes a significant reduction in the energy barrier associated with the cross-slip process. This phenomenon has been experimentally observed in H-charged Monel K-500 nickel-based superalloys [36]. By increasing the rate of cross-slip in the regions within a nanometer distance from the GBs, we can expect enhanced emission of vacancy clusters from the jogged dislocations. The direct MD simulations show the process of the divacancy emission in $\Sigma 33a$. Given the fact that this extra defect production mechanism only happens close to the GBs, the formation of the nanovoids and the increase in the free volume of them in the presence of H can be explained. Even without formation of nanovoids the extra vacancies created via this process damage the GBs. This damage decreases the cohesive strength of GBs and reduces the critical load for cleavage. This reduction, in addition to the reduction due to H coverage of free surfaces increases the susceptibility of the host metal to the intergranular brittle fracture. In this regard, hydrogen embrittlement happens when enhanced vacancy formation and free surface energy reduction take place. Although the calculations and simulations in this work are done for nickel, the mechanism for enhanced cross-slip can be relevant for GBs of other fcc metals in which segregated interstitial atoms are present.

ACKNOWLEDGMENTS

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DATA AVAILABILITY

The data that support the findings of this article are not publicly available upon publication because it is not technically feasible and/or the cost of preparing, depositing, and hosting the data would be prohibitive within the terms of this research project. The data are available from the authors upon reasonable request.

APPENDIX A: SIMULATION OF ADDITIONAL GBS

1. Effect of the loading rate on the simulation results

To demonstrate the critical role of the simulation loading rates on the results of the simulations, we examine the effect of the presence of hydrogen at the grain boundary on the nature of its interaction with the screw dislocation. To this end, we simulated the interaction of the screw dislocation with $\Sigma 9$, $\Sigma 33a$, $\Sigma 33b$, and $\Sigma 41$ GBs in the presence and absence of hydrogen. In these simulations, an increment of $\Delta\tau = 80$ MPa is applied at each 800 ps.

The key configurations of the dislocations interacting with $\Sigma 33b$ in different time steps are given in Fig. 7. In the H-free case, the dislocation starts to move towards the GB at $t = 0$ after the application of the first increment of loading. This motion continues, and the dislocation enters the GB at $\tau_{app} = 160$ MPa. No cross-slip is observed in the H-free case.

In the H-charged specimen, it can be seen that constrictions appear under $\tau_{app} = 160$ MPa. Then two dislocation segments cross-slip at $\tau_{app} = 480$ MPa ($t = 4.52$ ns). Here the cross-slip segment is limited to a finite length, and that segment acts as an obstacle for the glide of the whole dislocation. Due to the increase in the load, the dislocation starts to bow out. Figure 7(c) shows the configuration of the dislocation and GB at $\tau_{app} = 640$ MPa ($t = 6.4$ ns) in which the bow out is more visible. Eventually, the dislocation is unpinning and moves into the grain boundary at $\tau_{app} = 720$ MPa ($t = 7.2$ ns) through the formation of a dislocation loop around the cross-slipped segment, which was acting as an obstacle. The processes that the other grain boundaries undergo during the same loading conditions are quite the same and not presented here for the sake of brevity. In all H-charged cases, constrictions form along the screw dislocations and a segment of the dislocation cross-slips while the other segments tend to glide along the original glide plane. These segments bow out and form loops around the cross-slip segment and move toward the GB. The absorption of these dislocations at the GB happens at significantly larger loads (≈ 720 MPa) in comparison to the H-free cases (≈ 160 MPa). It is also noteworthy that the HECS is hardening the material, and the yield stresses are increased.

It is evident that although the cross-slip still occurs in this case, the details of the mechanism are entirely different. Note the fact that the loading rates in MD simulations are orders of magnitude higher than the experimental rates. Thus the results

of the simulations considered in this section are unlikely to happen in the real conditions. Thus we need to perform the incremental loads in a way that is described in Sec. III to preclude this weakness.

2. Hydrogen enhanced cross-slip in the vicinity of H-charged $\Sigma 9$ and $\Sigma 41$ GBs

In addition to the cases of $\Sigma 33a$ and $\Sigma 33b$ which are previously discussed, we simulated the dislocation GB interactions for $\Sigma 9$, and $\Sigma 41$. The details of the simulations are the same as discussed in Sec. III B. Figures 8(a) and 8(b) illustrate the key configurations observed corresponding to cross-slip events in the vicinity of $\Sigma 9$ and $\Sigma 41$, respectively. It is evident that the cross-slip is happening. These cross-slip events are not observed in any H-free case.

APPENDIX B: H-GB INTERACTIONS MODEL BASED ON LINEAR THEORY OF ELASTICITY

We adopt the Shockley-Read model for symmetric tilt GBs. This model of the low-angle GBs is represented as an array of dislocations. This model only accounts for the stress field of chemically clean GBs. The segregation of the H atoms to the GB is not considered at this stage. The elastic field of this array can be calculated via [66]

$$\begin{aligned}\sigma_{33}^{\text{GB}} &= -\tau_0 \sin(2\pi \bar{x}_2) (\cosh(2\pi \bar{x}_3) \\ &\quad - \cos(2\pi \bar{x}_2) + 2\pi \bar{x}_3 \sinh(\bar{x}_3)), \\ \sigma_{22}^{\text{GB}} &= -\tau_0 \sin(2\pi \bar{x}_2) (\cosh(2\pi \bar{x}_3) \\ &\quad - \cos(2\pi \bar{x}_2) - 2\pi \bar{x}_3 \sinh(\bar{x}_3)), \\ \sigma_{23}^{\text{GB}} &= \tau_0 (\cosh(2\pi \bar{x}_3) \cos(2\pi \bar{x}_2) - 1), \\ \tau_0 &= \frac{\mu b}{2S(1-\nu)(\cosh(2\pi \bar{x}_3) - \cos(2\pi \bar{x}_2))^2},\end{aligned}\quad (\text{B1})$$

where $\bar{x}_i$ indicates the normalization of x_i by the dislocation separation distance along the x_1 direction, $S = \frac{b}{2} \cot \frac{\Theta}{2}$, where Θ is the misorientation angle of the GB.

In order to model the segregation of the H atoms to the GB, we consider a 3D array of cuboidal inclusions with edge lengths a_i for $i = 1, 2, 3$ containing eigenstrain $\epsilon_{ij} = \epsilon \delta_{ij}$ (δ_{ij} is the Kronecker delta) embedded in an infinitely extended elastic domain as shown in Fig. 9(a). These inclusions are mimicking the misfit volumetric strain of an H atom in nickel. The periodic distances along the x_1 and x_2 directions are equal to $2L$ and the periodic distance along the x_3 axis is $2L_3 \gg 2L$. The first component of the displacement field, i.e., the component in the x_1 direction, associated with this array of inclusions, is given by [67]

$$u_1^{\text{inc}} = \frac{8c_H \epsilon (3\lambda + 2\mu)L}{\pi^4 (\lambda + 2\mu)} \sum_{m=1}^{\infty} \sum_{n=1}^{\infty} \sum_{r=1}^{\infty} \frac{\sin\left(\frac{\pi m x_1}{L}\right) \sin\left(\frac{\pi n x_2}{L}\right) \sin\left(\frac{\pi r x_3}{L_3}\right) \sin\left(\frac{\pi a_1 n}{L}\right) \sin\left(\frac{\pi a_2 m}{L}\right) \sin\left(\frac{\pi a_3 r}{L_3}\right)}{nr \left(\left(\frac{1}{L_3}\right)^2 r^2 + m^2 + n^2 \right)}, \quad (\text{B2})$$

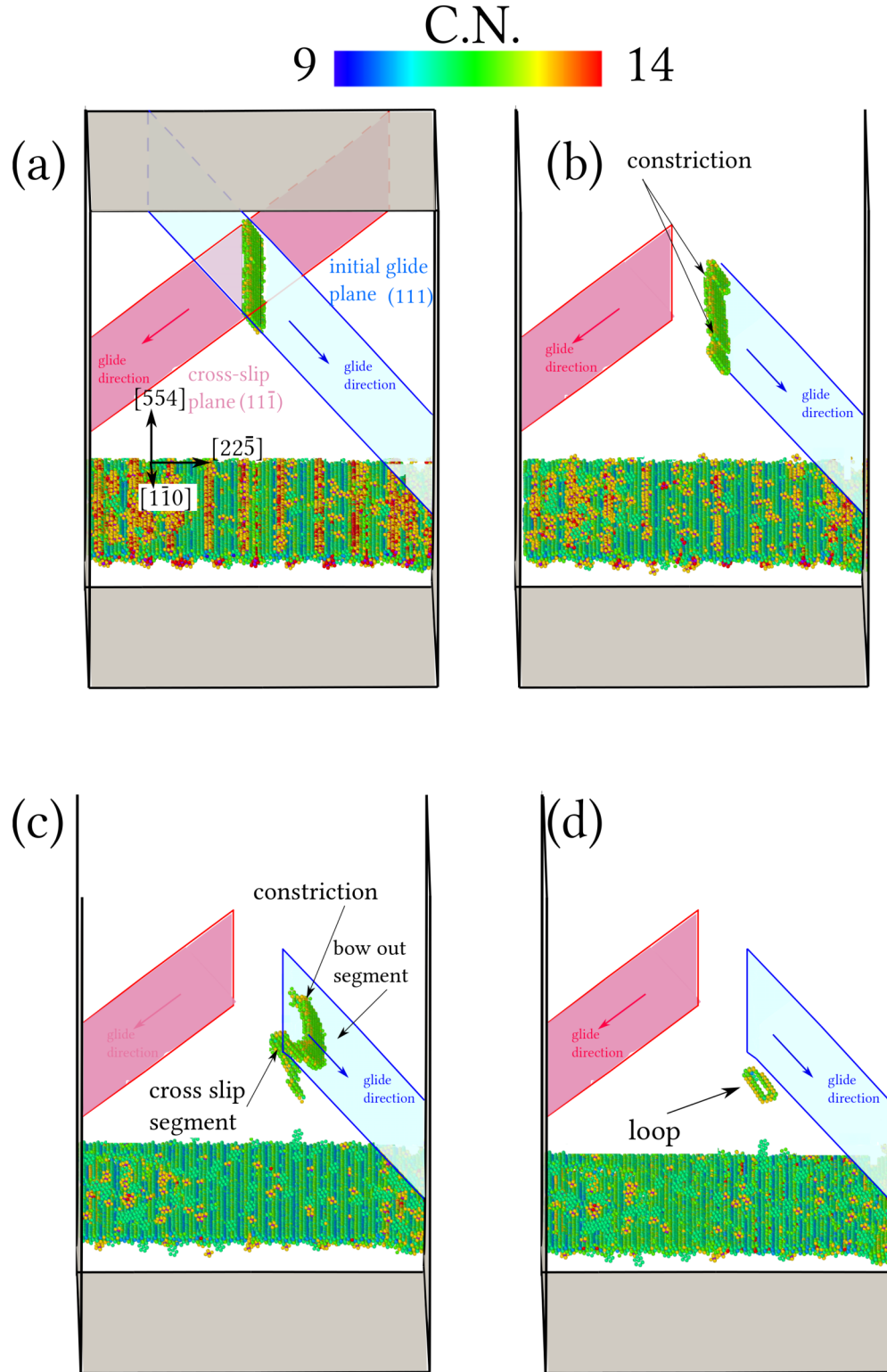


FIG. 7. The key configurations of the interaction of a screw dislocation with H-charged $\Sigma 33b$ GB: (a) initial configuration, (b) formation of the constrictions along the dislocation line at $t = 1.6$ ns, and (c) cross-slipped segments resist the glide of the other segments. Thus the dislocation bows out. The snapshot corresponds to $t = 6.4$ ns. (d) The dislocation is released from the self-established obstacle and enters the GB at $t = 7.2$ ns. The H atoms are highlighted as purple spheres, and the nickel atoms at the dislocation and GB are color-coded due to their coordination number (CN). The grey planes are aligned with the corresponding simulation cell boundaries and are given for guiding readers' eyes.

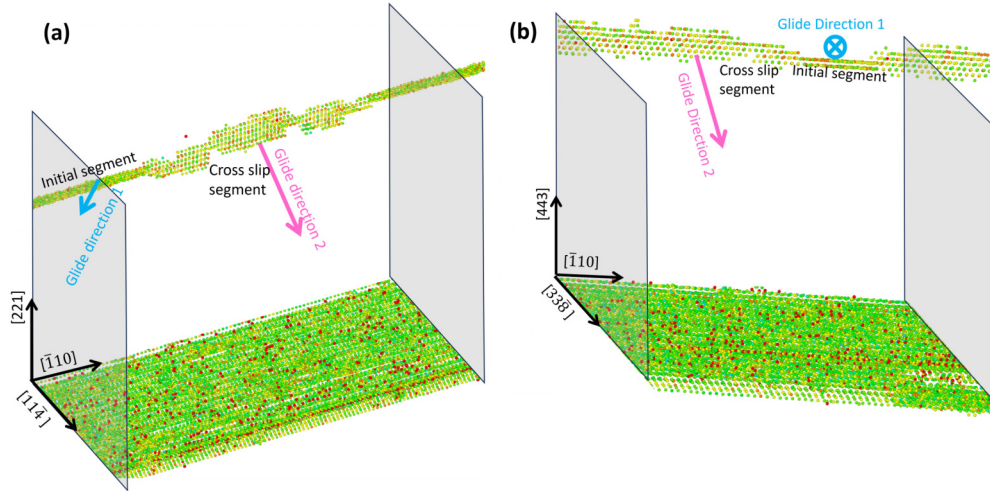


FIG. 8. Key configurations corresponding cross-slip observed in the reaction of a screw dislocation with (a) H-charged $\Sigma 9$ and (b) $\Sigma 41$. The H atoms are highlighted as red spheres, and the nickel atoms at the dislocation and GB are color-coded according to their coordination number (CN). The grey planes are aligned with the corresponding simulation cell boundaries as a guide to the eyes.

where λ , μ , and C_H are the Lamé constants of the matrix and the concentration of H at the GB, respectively. The other two components of the displacement field can be obtained by a permutation of m , n , and r . The stress field can be found using $\sigma_{ij}^{\text{inc}} = 2\mu\epsilon_{ij} + \lambda\epsilon_{kk}\delta_{ij}$ where $\epsilon_{ij} = \frac{1}{2}(\frac{\partial u_j^{\text{inc}}}{\partial x_i} + \frac{\partial u_i^{\text{inc}}}{\partial x_j})$.

Now the superposition of the stress fields of cuboidal inclusions representing the H atoms and a dislocation set representing the GB, i.e. $\sigma^{\text{tot}} = \sigma^{\text{inc}} + \sigma^{\text{GB}}$, gives rise to a first-order approximation for the stress state of an H-charged GB. This stress tensor is transformed to the local coordinate systems shown in Fig. 2(a) to find the Schmid and Escaig stress of each plane. These stresses are the input for Eq. (1) for calculating the energy barriers.

Figure 9(b) shows the value of E_b^* based on Eq. (1) for the case of our lowest angle GB $\Sigma 33a$ with a misorientation angle of $\Theta = 20.05^\circ$. The dislocation separation distance is $S = 7.08 \text{ \AA}$ and the periodic length of the inclusions is set to be $L = S/2$. We set $C_H = 1$. This choice takes into account the fact that most H atoms segregate to the dislocation core, and the concentration of them at the dislocation core is high.

The barriers are evaluated at $x_1/L = 0.5$ to capture the maximum effects. In this case, we use $a_1/L = 0.0$, $a_2/L = 0.5$, and $a_3/L = 1.5$, which are in accordance with the geometry of the H-segregated regions of the grain boundaries. The diagonal components of eigenstrain in the inclusion is set to be $\epsilon = 0.1$ to mimic the misfit volumetric strain of an H atom in nickel (≈ 0.3). Note that the low-angle boundaries are the boundaries with $\Theta \leq 15^\circ$, but since we are interested in the qualitative behavior of the barriers rather than quantitative values of them, we use this model as an approximation to the real situation.

It can be seen that the distribution of the regions with low barrier in the absence and presence of the inclusions (H atoms) is qualitatively in accordance with the results in Figs. 4(b) and 4(f), respectively. In the H-free case, the low barrier region is restricted to $\approx 10 \text{ \AA}$, which is approximately equal to $3L$. In the H-charged case, this region increases by almost an order of

magnitude ($30L \approx 90 \text{ \AA}$). Thus the increase in the eigenstrain of the GB due to the presence of interstitial H atoms, which are associated with large misfit volumetric strain $\approx 30\%$ is the main source for the formation of the low barrier regions in their vicinity.

Since the elastic anisotropy of nickel, the discrete nature of the GB structure at the nanoscale, and the spatial distribution of the H atoms are absent in this elastic model, we identify the misfit eigenstrain of H atoms as the main source for the substantially reduced barriers. A parametric study of the effect of the hydrogen concentration at the GB on the cross-slip barrier is given in Appendix B 1.

Effect of hydrogen concentration on at the grain boundary on the cross-slip barrier

In this section, we use the formulation given in B to analyse the effect of the concentration of the H atoms at the GBs on the reduction in cross-slip barrier. Here we change two free variables: one is C_H and a_1/l and keep all other input variables as given in B. Figure 10(b) shows the distribution of the normalized maximum width of the low-barrier region, i.e., $E_b^* = 0.7$ as shown in Fig. 10(a) versus C_H for different values of a_1/l . w is normalized to its value in the H-free case, namely, w_0 . In all cases, we can see that the width of the low barrier domain is increasing with increase of the concentration of H atoms within the cuboidal inclusion. The most significant increase is pertinent to $a_1/l = 0.5$. Interestingly both the increasing and decreasing a_1/l decrease the effect of H atoms in reducing the barrier to almost the same values. This observation indicates that the difference in the length of the H-free and H-charged regions along the dislocation lines of the GB is the main parameter that controls the effect of H in reducing the cross-slip barrier, and the maximal effect happens when the difference is zero, i.e. $a_1 = l - a_1$.

It should be noted that the concentration of the H atoms at the binding sites of the GB depends on the chemical potential

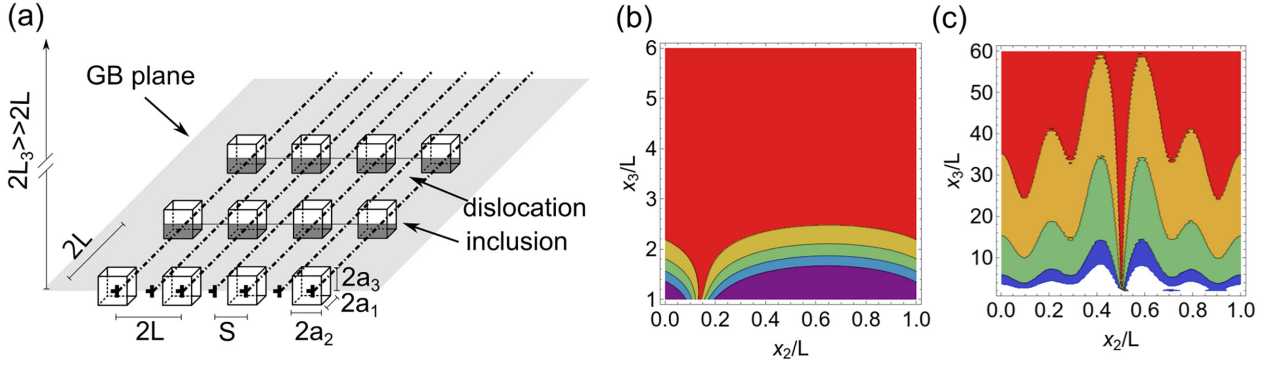


FIG. 9. (a) Schematic diagram of a general periodic array of inclusions and dislocations representing the segregated H clusters and GB microstructure, respectively. Variation of the calculated energy barrier E_b for the (b) H-free and (c) H-charged cases. The white color regions are the regions where Eq. (1) breaks down.. The periodic length L is 3.035 Å. Note the very different scale on the y axis in (b) and (c).

of H. Nevertheless, at experimentally relevant values of μ_H , corresponding to a bulk concentration of a few thousand at. ppm, these concentrations are typically between 0.5 and 0.9. This concentration ensures a significant effect of H concentration on the reduction of the barrier for cross-slip.

APPENDIX C: ESTIMATION OF THE INCREASE IN EXTRA VACANCY PRODUCTION DUE TO HECS

Estimating the total number of vacancies in the vicinity of the grain boundary requires a separate simulation, similar to the work of Li *et al.* [29], which considers not only vacancy production mechanisms like the one presented in this work, but also vacancy annihilation mechanisms such as those discussed in Ref. [30]. Nevertheless, we provide an estimation of the increase in vacancy production due to this mechanism. Consider a polycrystalline nickel sample with a mobile dislocation density of ρ_m . This implies that the dislocation separation distance can be estimated as $d = \rho_m^{-1/2}$ as shown in Fig. 11. If this sample is under tensile strain with a strain rate of $\dot{\epsilon}$ and a final strain of ϵ_f , then based on the Orowan relation, the dislocation glide velocity is $v_{\text{glide}} = \frac{\dot{\epsilon}}{b\rho_m}$, where $b = a_0/\sqrt{2}$ is the magnitude of the Burgers vector. The time that each dislocation neighboring the GB needs to travel from

its position to the GB vicinity is $t_{\text{glide}} = \frac{d}{v_{\text{glide}}} = \frac{b\sqrt{\rho_m}}{\dot{\epsilon}}$. The total time in the experiment is $t_{\text{tot}} = \frac{\epsilon_f}{\dot{\epsilon}}$, thus the number of dislocations arriving at the GB from each pile up with vertical spacing of d , is $n_d = \frac{t_{\text{tot}}}{t_{\text{glide}}} = \frac{\epsilon_f}{b\sqrt{\rho_m}}$. Given that the time scale for emission of the vacancies (≈ 2 ns) is far less than the traveling time of the dislocations (≈ 1 s), one can imagine that the dislocation emits γ_{vac} vacancies per dislocation length needed for their emission. This length can be estimated from our simulation box size as $L_{\text{seg}} \approx 50$ nm. Based on our simulations, the vacancy emission will take place at a distance of $h = 10$ nm from the dislocations. Thus the vacancy concentration per unit volume due to this production mechanism is:

$$C_{\text{vac}} = \frac{\gamma_{\text{vac}} \epsilon_f}{L_{\text{seg}} h b}. \quad (\text{C1})$$

The parameter $\gamma_{\text{vac}} = p_{\text{vac}} n_{\text{vac}}$ contains the information about the probability of emission per dislocation, p_{vac} , and the number of vacancies that a dislocation of length L_{seg} can emit, namely, n_{vac} . Given that the volume of a nickel atom is $v_0 = a_0^3/4 = \sqrt{3}2b^3/2$, the concentration of the

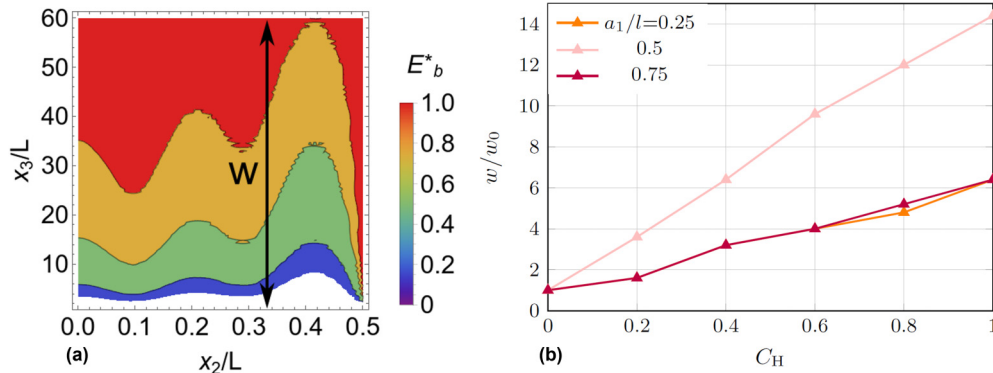


FIG. 10. (a) Same as Fig. 5(c). (b) Variation of the normalized width of the low barrier region versus the concentration of H atoms in the cuboidal inclusions. The normalization is performed with respect to the H-free case, i.e., w_0 corresponds to the H-free case.

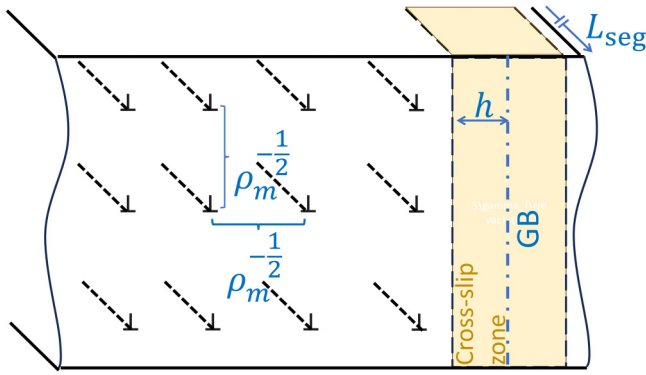


FIG. 11. Schematic configuration of the grain boundary and dislocations in polycrystalline nickel. The region in which the barrier for cross-slip is low is highlighted as yellow.

vacancies per nickel atom is

$$c_{\text{vac}} = \frac{\gamma_{\text{vac}} b^2}{L_{\text{seg}} h \sqrt{2}} \varepsilon_f. \quad (\text{C2})$$

For evaluation of this relation, we refer to Ref. [23], in which $\varepsilon_f \approx 0.15$. Thus $c_{\text{vac}} = 6.6 \times 10^{-7} \gamma_{\text{vac}}$. Given our presented mechanism the value of γ_{vac} is close to 1.0, but even if we use a conservative value of $\gamma_{\text{vac}} = 0.1$ due to scarcity of screw dislocations in total dislocation content of the material, we find that the total concentration of vacancies will be $c_{\text{vac}} = 6.6 \times 10^{-8} \gamma_{\text{vac}}$, which is orders of magnitude larger than the equilibrium vacancy concentrations in metals ($\approx 10^{-20}$ based on DFT calculations in Ref. [43]). This extra concentration of nonequilibrium vacancies in close vicinity to the GBs is detrimental and damages them.

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